THE DISPROPORTIONATION OF PROPENE ON SUPPORTED ORGANOMETALLIC CATALYSTS

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TO MY PARENTS

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ABSTRACT

The gas phase disproportionation reaction of propene on supported organometallic catalysts is described in detail. The catalysts studied during the research were based mainly on molybdenum and tungsten, and were supported on a variety of oxides. A static vacuum system was employed in the catalysis and the reproducibility of catalyst activities was guaranteed to a large extent by the development of an "in situ" preparation technique.

The molybdenum hexacarbonyl catalyst was studied in close detail using a series of supports and the effect of varying the pretreatment of support indicated a maximum in activity attributable to the appearance of certain surface hydroxyl groups. Study of the activation temperature of these supported catalysts suggested that the active species contained no carbonyl groups and that the molybdenum had undergone oxidation from Mo(O) to a higher oxidation state during the process of activation. Infrared and e.s.r. spectroscopic techniques were used to support the findings of the kinetic experiments.

The activities of a series of molybdenum and tungsten non-carbonyl complexes supported on alumina and silica were measured using the same mode of catalyst preparation. The considerable activity of such catalysts was a consequence of the rapid decomposition of the complex on the support and formation of the active species by oxidation. In the case of the hexamethyltungsten catalyst it is thought that the active catalytic species is generated by a reduction process.

CONTENTS

CHAPTER ONE

INTRODUCTION

1.1 Historical Background

The term catalysis (which is derived from the Greek 'katalysis' meaning breaking down or loosening) was introduced in its present meaning in 1836 by J.J. Berzelius[1] who assembled the results obtained from earlier workers. Berzelius assumed that certain substances called catalysts exerted a special catalytic force upon the reactants in a chemical reaction. This force was not expected to hold any mystical connotations and Berzelius himself was prepared to consider it no more than a display of electrochemical affinity of some description. A more detailed definition of this force was proposed by W. Ostwald[2] in 1902. Ostwald had witnessed the development of physical chemistry, especially the discovery of the theory of reaction rates and the laws of chemical equilibrium, and as a result, catalysis had become a kinetic phenomenon. He defined catalysts as "agents that speed up chemical reactions without affecting the chemical equilibrium". Despite the fact that it is not completely precise and that it is only valid for reversible reactions, this definition is probably the most frequently cited.

P. Sabatier[3] recognising that Ostwald's definition did not include any form of autocatalysis, considered catalysis simply as "a mechanism, causing or accelerating, certain chemical reactions by substances which themselves are not irreversibly altered". This definition is less restrictive than

Ostwald's, but unduly stressed that catalysts must not undergo irreversible changes during reaction. Most catalysts, however, become inactive due to side reactions or contaminants. As knowledge of the theories of reaction rates increased, it was clear that the energy of activation of a reaction was lowered in the presence of a catalyst. Expanding on this useful enough definition, it must be outlined that the lowering of the activation energy occurs through the direct interaction of the catalyst with the substrates. There are examples, however, where so-called catalytic reactions are observed, where there is no such direct interaction. In the case of enzyme reactions, the addition of sodium ions, which constitute non-stoichiometric additives, may enhance the rate of a reaction indirectly by causing conformational changes of the enzyme protein without actually playing a key role in the chemical conversion of the substrates. It would be pedantic not to describe such additives as catalysts since a religious definition of the latter is not always possible.

An up-to-date definition of a catalyst should embrace the qualities ascribed to that entity during the early years of its role in physical chemistry, allied to the information obtained from modern kinetic and equilibrium studies.

1.2 A Definition

A catalyst is a substance that increases the rate at which a chemical process occurs. It can increase the rate of only those reactions which are thermodynamically feasible. The equilibrium position attained when a catalyst is present must

be the same as that accomplished in the absence of the catalyst, and any change which the catalyst causes in the rate of the forward reaction must be accompanied by a similar change in the rate of the back reaction. A catalyst should still be effective when present in small proportions relative to the reactants. Catalysis is the term used to describe the action of a catalyst.

In general terms, catalysed reactions can be divided into two main classes:-

(i) Homogeneous catalysis in which the catalysts and reactants are in the same phase.

(ii) Heterogeneous catalysis in which the reaction takes place at an interface between two phases.

In this thesis, we shall be solely concerned with heterogeneous catalysis involving reactions occurring at interfaces between supported organometallic catalysts and olefins, although it is worthwhile to point out that the olefin disproportionation reaction of heterogeneous catalysis[4] has a complementary reaction in homogeneous catalysis, olefin metathesis[5].

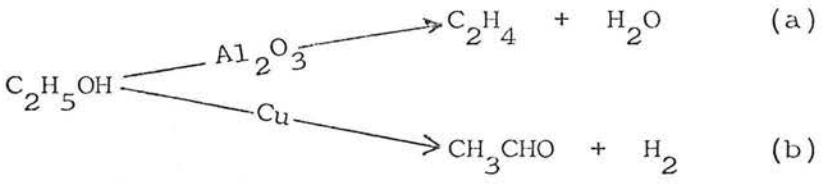
1.3 Heterogeneous Catalysis

During the last century, two theories were proposed as explanations into the results obtained from considerable investigations into heterogeneously catalysed chemical processes.

The first of those theories was that of mechanical impact whereupon the catalyst was subject to collisions with the reactant molecules forming intermediates which subsequently broke down to give products of the main reaction with regeneration of the catalyst. This theory, at the time, appeared to fit the experimental data presented for most catalytic processes due

mainly to changes in the catalyst surfaces. However, the theory failed due to the absence of direct evidence for the formation of bulk intermediates.

This theory was superseded by a "contact action" theory proposed by Faraday[6] whereby physical forces of attraction between the catalyst and the reactant brought about increased reaction rates, chiefly because of increased concentrations of reactants in the condensed layer. The specificity of catalytic reactions could not be explained by such a theory considering only physical forces of attraction. This is exemplified by considering the decomposition of ethanol over alumina and copper at 573K.



In the case of alumina, i.e. (a), the observed products are ethylene and water, viz dehydration. In the case of copper, i.e. (b), the products are acetaldehyde and hydrogen, viz dehydrogeneration.

These findings led Sabatier[3] to consider the concept of unstable surface compounds acting as intermediates in heterogeneous catalysis.

Langmuir[7] endorsed these considerations by his work on adsorption. He proposed that the reactant gaseous molecules were being held by short range forces at the surface and moreover they were being held at certain specific sites on the catalyst. He felt that the bonds holding the reactant molecules to the surface were chemical in nature and were limited by the number of sites available on the catalyst. Langmuir[8] introduced

equations which related the amount of gas adsorbed to the pressure in the gas phase and these equations have proved to be of great value in the understanding of the kinetics of many catalytic reactions.

1.4 Adsorption

When two immiscible phases are brought into contact, it is nearly always found that the concentration of one phase is greater at the interface than in its bulk. This tendency for accumulation to take place at the surface is called adsorption. Its occurence is due to the atoms in any surface being subject to unbalanced forces of attraction perpendicular to the surface plane, and therefore possessing a certain unsaturation. During chemical reactions, at least one of the reactants must be adsorbed upon the catalyst surface and adsorption experiments have shown that there are two main ways in which the reactant can achieve surface adsorption. These types of adsorption are referred to as physical adsorption and chemisorption.

Physical Adsorption

In the case of physical adsorption, the molecules are held to the surface of the catalyst by attractive Van der Waals forces - similar in magnitude to the forces employed in holding a liquid together. The heats of adsorption are generally very low - comparable to the heat of condensation of the adsorbing gas. Physical adsorption only occurs at very low temperatures, similar to that of the boiling point of the adsorbate and it can be multilayer in nature. The rapid rates of adsorption and desorption render this type of adsorption useful in determining

the values of some of the surface properties of catalysts, e.g. the measurement of surface areas[9] and pore size distributions[10]. There have been cases where physically adsorbed species take part in catalytic reactions[11] but this type of adsorption is not generally used to explain catalysis.

Chemisorption

The process of chemisorption[12] involves the interaction between the electrons of the adsorbent and those of the adsorbate, with the formation of bonds of the strength associated with chemical compounds. The process occurs when the atoms at a surface form bonds with the nearby phase rather than with the neighbouring surface atoms. Chemisorption can take place at liquid surfaces, especially if the adsorbed molecules are ionized, but generally interest has centred around the chemisorption of gases and vapours on solid surfaces.

Chemisorption is distinguishable from physical adsorption in various ways although one must beware of making too rigid generalisations. Chemisorption can be characterised by high heats of adsorption in the range of 80 kJ mol^{-1} to 200 kJ mol^{-1} although hydrogen adsorption has been detected[13] with a heat of adsorption in the region associated with physical adsorption. Normally chemisorption ceases after monolayer coverage since the unsaturated sites are no longer accessible to the adsorbate molecules. Chemisorption is usually observed at temperatures far above the boiling point of the adsorbate although it has been detected at lower temperatures in certain cases[14]. Rapid adsorption need not be indicative solely of physical adsorption since rapid chemisorption can occur due to a surface

which is extremely clean and unsaturated[15]. Chemisorption is specific and, unlike physical adsorption, it will not occur unless a surface is clean and unsaturated. The type of bond formed during chemisorption is important in catalytic reactions. If the adsorbate is too strongly held, then the surface may well become poisoned. Also, if the bond is a particularly weak one, then the adsorbate will not be held long enough to the surface to undergo reaction.

The intermediates formed by chemisorption are the subject of increasing study by workers in catalysis. Magnetic measurements[16,17] have provided useful pointers and more recently infrared techniques have proved useful tools[18,19].

1.5 Mechanism of Surface Reactions

A catalytic reaction will proceed via chemisorption of at least one of the reactants. It is well established that surface reactions can be visualised as involving five consecutive processes:

(i) Diffusion of the reactants through the gas phase to the surface.

(ii) Chemisorption of at least one of the reactants.

(iii) Reaction on the surface.

(iv) Desorption of the products.

(v) Diffusion of the products away from the surface.

The slowest of these processes is regarded as the rate determining step of the catalytic reaction. It is normally thought that steps (i) and (v) are not the rate determining steps. Diffusion controlled reactions arise mainly in liquid reactions or in the catalysis on solids where porous catalysts

are being used. It can be determined if a reaction is diffusion controlled by measuring the rate of reaction at various temperatures and studying the Arrhenius plot. If a straight line is obtained, then the reaction is not diffusion controlled.

Step (iii) - the surface reaction is thought to proceed mainly by one of two proposed mechanisms. These mechanisms are the Langmuir-Hinshelwood mechanism[20,21] and the Eley-Rideal mechanism[22,23].

The mechanism developed by Langmuir and Hinshelwood involves the surface reaction of two adsorbed species. The adsorbed species are in equilibrium with the gaseous reactants and these species are chemisorbed on adjacent sites. Some controversy arose when Roberts[15] noticed that although hydrogen was readily adsorbed on tungsten at temperatures well below 273K, its desorption occurred only with great difficulty at temperatures around 673K.

This led Eley and Rideal to propose a mechanism which involved the chemisorption of one of the reactant molecules and subsequent reaction with another physically adsorbed reactant molecule on an adjacent site. This mechanism is not as commonly accepted as the Langmuir-Hinshelwood model.

The most accurate description of a surface mechanism is extremely difficult to determine and spectroscopists are playing a vital role in understanding the types of surface intermediates involved in catalysis. E.s.r. is an extremely useful tool in this respect[24] and infrared spectroscopy[19] has answered several questions in this field during recent years. Tracer studies[25] have been extremely helpful in aiding one's search for insight into catalytic reactions.

1.6 Catalysts and Catalytic Activity

Catalysis at the interface between solids and gases is a complex phenomenon and although there is no particular theory which is able to predict the activity of catalysts in an all-embracing manner, it has proved useful to explain the activity of catalysts by two factors, viz the "geometric factor" and the "electronic factor".

The "geometric factor" involves considerations of the structure of the surface and this has been employed to explain the catalysis of systems involving large molecules. An example of this was described[26] in which the reactant benzene molecule was required to lie flat on the surface to accommodate the geometry of the surfaces of various transition metals. More recently[27] the geometric factor was related to crystal field stabilisation in the adsorption of oxygen on nickel oxide and the conclusion was drawn that the different crystal faces have different catalytic properties. However, the "geometric factor" alone is unable to explain the workings of complex catalytic reactions.

The "electronic factor" is more relevant and directly applicable to catalysis[28]. This involves a more intimate relationship between the bulk solid and the adsorbate molecules by considering electron transfer between the two phases. It is well established that transition metals have a higher activity than non-transition metals and it has been proposed that the reason for this was the vacant d-orbitals of the former[29]. Alloys have served a useful purpose in correlating catalytic activity with the structure of the d-band[30]. It is not

possible to explain activity entirely by this "electronic factor" and its validity has met with criticism[31]. Rather than consider the electronic structure of the bulk, it has been suggested that investigations of the properties of the individual atoms or complexes at the surface would be more fruitful[32].

It is generally accepted that the explanation of catalytic activity involves the combination of these two factors, and indeed, one may complement the other. The role of some transition metals in certain catalytic reactions such as olefin disproportionation[33] and double-bond isomerization[34,35] involves the consideration of both of these factors. In the case of disproportionation, the metal acts as a geometric template in the positioning of the two reactant molecules whilst at the same time the metal orbitals provide a pathway whereby fluid interchange of electrons can occur between the metal and the reactant molecules, thus enabling a smooth rearrangement of the electron distribution.

Catalysts can be prepared in a large number of ways, the final form of the catalyst being important in its role during a catalytic reaction. Catalysts can be used in their bulk form, e.g. as evaporated films, wires, powders, and foils with particular emphasis on the surface area and pore size distribution of that particular catalyst. A catalyst can also be presented in a way in which it is supported on a carrier. A carrier is defined[36] as "a substance which has no catalytic activity of itself, but when a metal is supported on its surface, the physical and mechanical properties of the resulting catalyst are superior to those of the unsupported metal". It would appear

from this definition that the carrier merely assumes a passive role. Work has been completed, however, which seems to disprove this viewpoint[37].

In the work presented in this thesis, it will be noticed that the part played by the support is intrinsically important in the catalytic reaction.

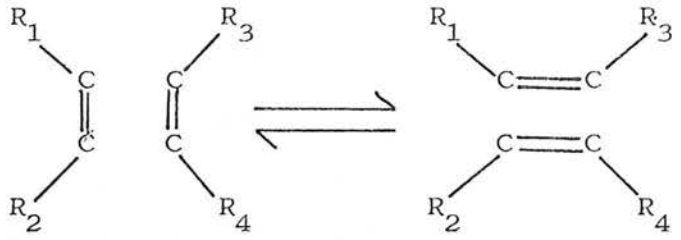
CHAPTER TWO

DISPROPORTIONATION OF OLEFINS

"Certainly the most intriguing catalytic reaction to be discovered in this decade" F.D. Mango (1970)

2.1 Introduction

The reaction in which olefins are converted to homologues of shorter and longer carbon chains is called disproportionation. This process can be exemplified by a reaction of the type:-



In this catalytic reaction, carbon-carbon double bonds are broken and made with striking ease allowing a smooth olefin interconversion.

The term disproportionation implies a process involving the formation of dissimilar parts. It can be seen from the above process that the reaction may involve the formation of similar entities and, although in 1964 Banks and Bailey[4] introduced this novel reaction pathway under the heading of "disproportionation", the seemingly misleading nature of this terminology induced certain workers[5] to name it"olefin metathesis" which is thought to convey properly the nature and scope of the reaction. Most homogeneous work appears under this latter heading, but it is not surprising that both heterogeneous and homogeneous systems should be described under the title of "olefin dismutation".

In heterogeneous catalysis, the process has retained its original terminology - "disproportionation of olefins".

Since this new reaction made its impact in 1964 there has been a great deal of research into the catalytic system both heterogeneously and in the homogeneous phase. This research has involved the development of disproportionation catalysts as well as an increase in the number of syntheses afforded by the process. Disproportionation of olefins was reviewed by Bailey[38] and since that publication the more recent advances in this field have been assembled and reviewed by certain Russian workers[39] in 1971, and also by Calderon[40] in 1972. The work which has been reported during the last decade has taught us a great deal about the catalytic system without firmly pinning down the exact mechanism of the reaction. After Banks and Bailey in 1964, it was proposed[41] that the reaction proceeded via a four-centred intermediate - commonly called a "quasi-cyclobutane" intermediate. This structure, however, has been the subject of great controversy during the past five or six years, and has been referred to in that time as "pseudocyclobutane",[42] "adsorbed cyclobutane",[43] and "cyclobutane".[5,34] The mechanism of the reaction will be discussed more fully in Section 2.5.

2.2 Heterogeneous Catalysts

The original publication[4] described the use of catalysts based mainly on molybdenum and tungsten. In the disproportionation of low molecular weight linear olefins, the catalysts employed were molybdenum and tungsten hexacarbonyl and molybdenum trioxide. All were supported on alumina. Since that

research was carried out, the number of disproportionation catalysts has increased sizably. The catalyst systems are composed mainly of a "promoter" and a "support". Generally, the catalyst consists of the promoter deposited on the high-surface-area refractory support although it is dangerous to assign one or the other of these terms to a catalyst component since they may only be distinguishable by their respective weights. Their exact functions in the catalyst system are not fully understood.

Table 2.1[38] presents most of the catalytic systems which have been employed for heterogeneous olefin disproportionation. It would be quite acceptable to trim this list down to a select few catalysts, since it is with these systems that most of the research has been carried out: the oxides and carbonyls of molybdenum, tungsten and rhenium and cobalt molybdate. Generally the support material has been silica or alumina.

Silica-alumina has been employed as a support[44] for a tungsten trioxide system and the catalyst was highly active in the temperature range 533 - 598K. The cracking qualities of this support appeared to be present since the equilibrium conversion of propene was ~50% - thus other reactions were taking place. Since 1964 some study has been made of the modes of preparation. The various catalysts have been prepared in a number of ways and patent literature has described the variations quite fully. Impregnation is possibly the technique most widely implemented. The preparation described[4] for molybdenum oxide on alumina involves the impregnation of an alumina with an aqueous solution of ammonium molybdate, the alumina having undergone a prescribed pretreatment. The resultant

TABLE 2.1

HETEROGENEOUS DISPROPORTIONATION CATALYSTS

	Supports			Promoters			
Oxides	Al	Si	Fe	Mo	W	Re	
	Ni	Zr	Sn	Nb	Rh	Sn	
	W	Th	SiAl	Te	La	Ta	
	AlTi	AlTh	MgSi	Os	Ir		
	MgTi						
Phosphates	Al	Ti	Ca	Ti	Zr	Nb	Ta
	Zr	Mg		Mo	W	Re	
Hexacarbonyls				Mo	W	Re	
Sulfides				Rh	V	Nb	
				Mo	W	Ta	
Halides				Ti	Zr	Nb	Ta
				Mo	W	Re	
Sulphates				Ti	Zr	Nb	Ta
				Mo	W	Re	

compound was converted to the oxide by calcination. The preparation of a tungsten oxide-silica catalyst is described[45] whereby an aqueous ammonium metatungstate solution was added incrementally to 20- to 40-mesh silica gel. Between additions a steam bath was used to dry the wet mass. This catalyst was activated with dry air at~930K for 1 hour before use. The preparation of hexacarbonyl catalysts[4,46] involved impregnation of the alumina support with a solution of the hexacarbonyl in a suitable organic solvent, e.g. cyclohexane. Silica may also be used as a support for the hexacarbonyls. The preparation of dirhenium decacarbonyl on alumina[47] involves an extensive procedure in which the alumina is modified by treatment with mineral acid before its impregnation by the carbonyl solution. Other preparative methods include dry-mixing and co-precipitation.

After the preparation of the catalyst, there is generally an activation procedure which is carried out before the catalyst is tested for activity in disproportionation reactions. This procedure may take the form of heating the support in order to remove adsorbed water and thus generate certain "active sites" before the addition of the solution of the catalyst. The procedure may involve treating the catalyst at an elevated temperature in an attempt to form a configuration of the promoter on the support which may render the catalyst active. This is particularly common in the case of oxide catalysts.

The activation of the catalyst or support may not always involve heat. There are certain examples where a disproportionation catalyst is treated with alkali metal ions[41,48] in an attempt to modify the selectivity of the catalyst. The

selectivity of the catalyst towards disproportionation is increased by poisoning the sites responsible for double-bond isomerization. Various other cations and anions have been reported as having properties which enhanced the activity of catalysts in disproportionation; e.g. copper and silver ions in molybdenum and rhenium catalysts and sulphate, phosphate and fluoride ions in rhenium oxide catalysts. The effect of exposing the catalyst to certain gases has been studied and oxygen, carbon monoxide and air have been reported[49,50] as being successful in promoting the activity of catalysts. Such promoters are also known to poison catalysts under certain conditions. Fluorinated and chlorinated olefins have been reported[51] as having an activity-enhancing effect on a molybdenum hexacarbonyl on alumina catalyst. These halogenated olefins were exposed to the catalyst in the form of gases.

Table 2.2 presents examples of the conditions used by various workers[38,46] for the disproportionation of propene over the more common catalysts. Obviously the activation and reaction parameters can be varied widely and it is extremely difficult to compare directly the activity of different catalysts in different systems prepared under dissimilar conditions. The temperature of reaction is perhaps the most useful parameter in judging catalyst activities. Whereas rhenium oxide is a low temperature catalyst (below 370K)[52], molybdenum and tungsten oxides are higher temperature catalysts with the tungsten oxide on silica catalyst used extensively at extremely high reaction temperatures (~720K). Generally silica supported catalysts take on the role of high-temperature catalysts. Hexacarbonyl catalysts are active at low temperatures (300K) but, depending on their preparation, their

TABLE 2.2

RESULTS FROM VARIOUS DISPROPORTIONATION CATALYSTS

Catalyst	14% Re_2O_7 on alumina	3% $Mo(CO)_6$ on alumina	5% MoO_3 on 95% $AlPO_4$	3.4% CoO 11% MoO_3 on alumina	3% WO_3 on silica
Test Conditions					
Temperature/K	298	393	813	438	698
Pressure/p.s.i.g.	0	500	100	450	450
Space Rate/g/ghr	6		7.5	8.5	40
Propene Conversion/%	30.2	25.0	34.0	43.0	45.0
Efficiency to Ethylene and Butene/%	100	97	82	94	98

activity can be promoted at reaction temperatures up to 410 to 500K.

2.3 Homogeneous Catalysts

The homogeneous catalysts at present available which are capable of catalyzing the disproportionation of olefins are mainly based on complexes of molybdenum and tungsten.

Calderon and co-workers[5,53] began the study of the homogeneous catalysis of this reaction by using a new catalytic system consisting of tungsten hexachloride, ethanol and ethyl aluminium dichloride in benzene. It was observed that for olefin metathesis, equilibrium conversions were obtained in less than two minutes at room temperature. None of the components of the system were found to be individually active for this reaction, although the activity of the catalyst system was markedly decreased in the absence of ethanol. The Al:W ratio was varied within wide limits but optimum results were achieved on Al:W ratio of 4:1. This system was extremely effective in the disproportionation of C_4 and higher olefins with a non-terminal double bond. The selectivity was very high, reaching 99.6% in the case of pent-2-ene, but-2-ene and hex-3-ene. This system was handicapped by oligomerization which decreased in the order :

but-2-ene > alk-2-ene > alk-3-ene > alk-6-ene

Oligomerization was obviously dependent on the position of the double bond.

Wang and Menapace[54] developed a system in which oligomerization was absent. They employed a binary catalyst of tungsten

hexachloride and n-butyl lithium which was extremely selective in the 100% conversion of pent-2-ene to but-2-ene and hex-2-ene. The n-butyl lithium component acted as an alkylating and reducing agent for the tungsten hexachloride. It was found that the system only catalyzed the disproportionation of pent-2-ene effectively with a Li:W ratio of 2:1. By replacement of the n-butyl group with sec- and tert-butyl, it was found that the conversion of pent-2-ene decreased in the order:

n-butyl > sec-butyl > tert-butyl.

Zeuch and Hughes[42,55,56] have been mainly responsible for the development of a homogeneous catalytic system containing nitrosyl complexes of the type $L_2Cl_2(NO)_2M$ (where M = Mo, W and L = $(Ph)_3P$, C_5H_5N, PH_3PO and others). This complex, when treated with alkylaluminium chlorides in chlorobenzene proved to be a very effective catalyst at low temperatures (273 to 323K). The activity of these nitrosyl-containing catalysts depended on the metal, molybdenum compounds being more active than their tungsten analogues. Molybdenum compounds also proved to be more selective than tungsten compounds. Catalysts of the type $L_2Cl_2(NO)_2M$ were found to be extremely useful in the disproportionation of α,ω dienes.

Ugo[57] has also reported the homogeneous disproportionation of olefins by using the chromium complex benzene chromium tricarbonyl.

2.4 Reactants

A wide range of unsaturated reactant molecules has been studied in the disproportionation of olefins. The different groups of reactants can be divided into four classes:

(1) Acyclic mono-olefins

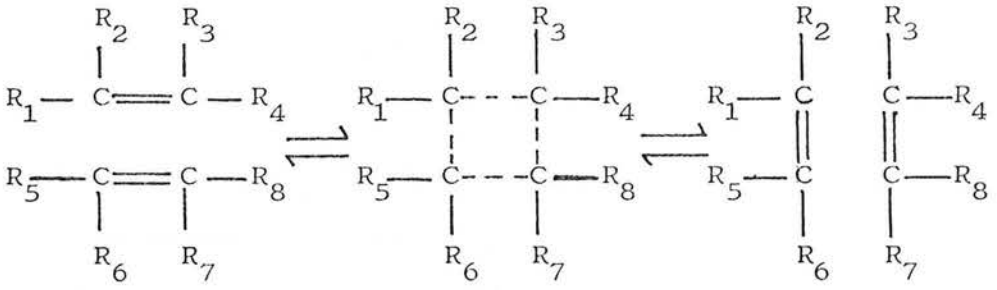
(2) Di-olefins

(3) Cyclic olefins

(4) Alkynes

Acyclic Mono-Olefins

Most of the work reported for olefin disproportionation has been carried out using mono-olefins of carbon content C_3 to C_8. The reaction is thought to proceed as indicated below, the products being explained in terms of the four-centred mechanism.



In addition to the olefin disproportionation reaction, products are observed over certain catalysts that can be explained by attendant isomerization and polymerization processes. These side-products may upset the product distribution obtained from the disproportionation reaction. If allowances are made for such side-reactions, the main disproportionation products become clear.

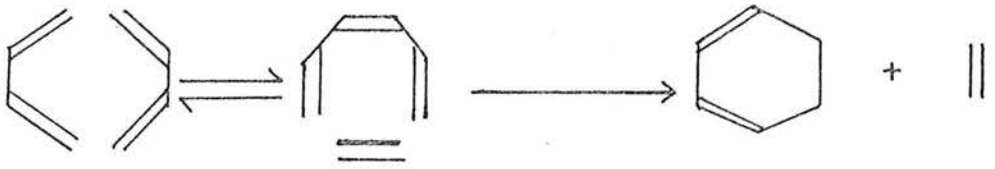
No disproportionation occurs if the two alkyl groups joined by the double bond in each reactant are the same. However, the proposed mechanism can be detected if labelled symmetrical molecules are used. Calderon and co-workers[53] demonstrated that, in a homogeneous system, the disproportionation of but-2-ene (d_o) and but-2-ene (d_8) which produced but-2-ene (d_4) in the

products, indicated the exchange of identical structures and the presence of the four-centred mechanism.

Propene has been employed in heterogeneous disproportionation processes more than other olefins, and this is probably since the products from the reaction, ethylene and but-2-ene, are observed with little difficulty. The appearance of secondary products relies mainly on the isomerization of the butene.

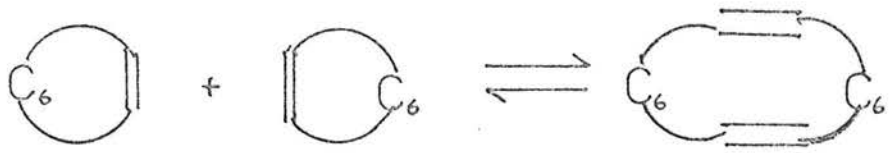
Di-Olefins

The validity of the four-centred mechanism was tested[58] by studying the disproportionation of di-olefins over a tungsten oxide on silica catalyst, treated with sodium carbonate to reduce isomerization and polymerization side-reactions. The reactions of 1,3-butadiene, both alone and with a range of mono-olefins of carbon content C_3 to C_5, were studied at 811K. Butadiene reacted over this catalyst to give ethylene and cyclohexadiene. If this reaction were to proceed via a four-centred mechanism, ethylene and hexatriene would be the expected products. However, under these experimental conditions, isomerization of hexatriene took place and cyclohexadiene was formed.

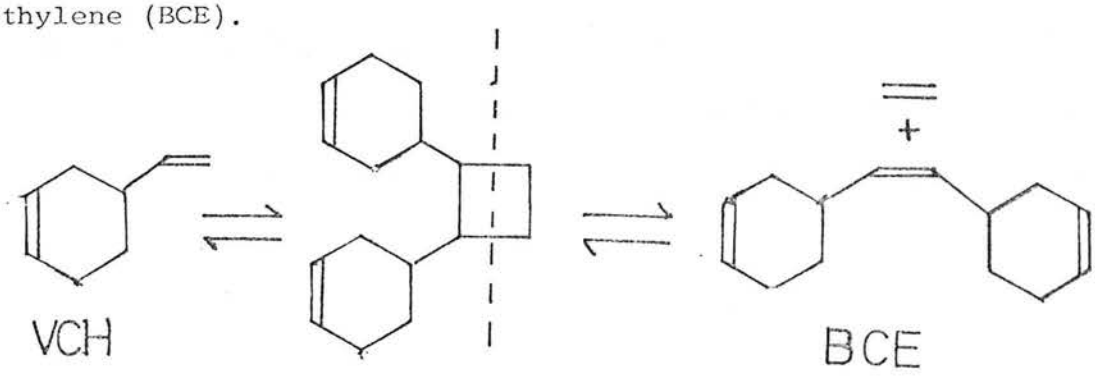


The products of the reaction of 1,3-butadiene with the range of mono-olefins agreed completely with those predicted from a four-centred mechanism.

Workers at British Petroleum[59] used a rhenium oxide on alumina catalyst in the disproportionation of cyclo-octene. The products of this reaction included cyclohexadecadiene, which seemed to suggest the involvement of a four-centred mechanism.



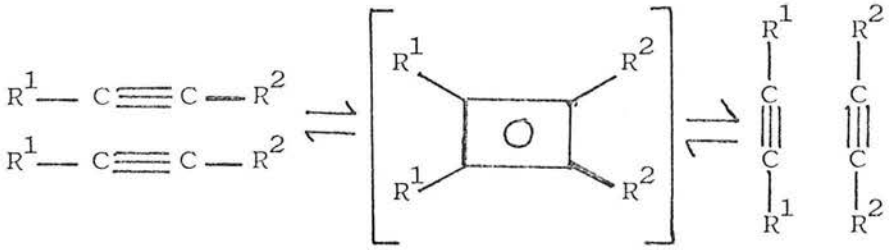
Crain[60] demonstrated the application of this route in the disproportionation of 4-vinylcyclohexene (VCH) over a molybdena-alumina catalyst at 373 - 423K. VCH, which has a vinyl double bond and a ring double bond, is thought to form a four-centred intermediate which breaks down in the expected fashion to form the main products, ethylene and 1, 2, bis (3-cyclohexenyl) ethylene (BCE).



Crain demonstrated that the vinyl groups on VCH were more reactive than the double bonds within the ring. He also studied the ethenolysis of cyclic olefins and noticed the formation of α,ω dienes. Ethenolysis is a term often used to describe the reverse reaction of disproportionation, viz the cleavage of one olefin by ethylene.

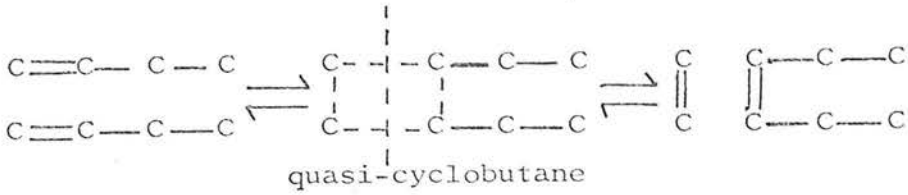
Alkynes

The disproportionation of acetylene was first postulated[61] when acetylene and deuterated acetylene were photolysed. A four-centred mechanism was proposed at that time, and this proposal was repeated[62] when pent-2-yne was allowed to react over a tungsten oxide on silica catalyst and a four-centred mechanism appeared to explain the product distribution.



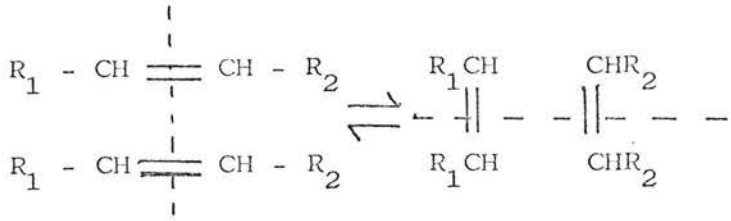
2.5 Mechanism and Kinetics

The concept of a four-centred mechanism was first introduced by Bradshaw and co-workers[41] who studied the disproportionation of but-1-ene over a cobalt molybdate catalyst. It was noticed that the selectivity to ethylene and hexene varied inversely as the isomerization of but-1-ene to but-2-ene. These workers then treated the catalyst with sodium bicarbonate and by successfully poisoning the sites available for isomerization a more selective disproportionation reaction to ethylene and hexene was detected. The reactions of ethylene with cis-but-2-ene and 4-methyl-2-pent-ene were studied and all of the results seemed to indicate that the disproportionation reaction was proceeding via a four-centred intermediate, which Bradshaw and his co-workers called a "quasi-cyclobutane" structure.



quasi-cyclobutane

Calderon[5] explained the homogeneous reaction in terms of a transalkylidenation mechanism:



and not by a transalkylation process. Mass-spectral studies[53] showed that transalkylation was not involved in olefin disproportionation.

The validity of the "quasi-cyclobutane" intermediate was investigated[63,64] by using C^{14}-labelled propene. By initially incorporating the isotopic carbon in the 2-position, it was found that all the labelled carbon appeared in the butene product, thus ruling out a linear mechanism[65]. A π-allyl mechanism was excluded since the methyl groups retained their identity throughout the disproportionation process. Calderon[53] also tested the validity of the four-centred mechanism by conducting experiments with 2-butene-(d_8). On reacting this species with the unlabelled 2-butene-(d_o) and hex-3-ene it was found that in both cases only one new product was obtained, which had a mass consistent with the four-centred mechanism.

The exact nature of the four-centred intermediate has been the subject of much discussion since its initial proposal[41]. Mol[65] opined that the intermediate was in the form of a cyclobutadiene which had been formed as a result of hydrogen abstraction. This assertion has been challenged by Crain[48]

who carried out several experiments with a molybdena-alumina catalyst treated with potassium hydroxide. Conclusive proof that the "Mol-type" cyclobutadiene intermediate had not been formed was presented in the ethenolysis of 2,3-dimethyl-2-butene. Isobutene was the sole product. If the cyclobutadiene intermediate had been present, then two methyl groups and two hydrogen atoms would have had to migrate to the catalyst and return to the same carbon atoms. Since there had been no detection of methylbutenes, propene or n-butenes in the products it would seem that there was no possibility of a cyclobutadiene intermediate. Calderon's[53] experiments with deuterated but-2-ene seemed to rule out a cyclobutadiene scheme in the homogeneous system, since a random distribution of hydrogen and deuterium on carbons 2 and 3 of butene was not observed. Mol[67] reported further results from the disproportionation of 2-deuteropropene over a rhenium oxide catalyst and by the fact that there was no deuterium in the ethylene product, it seemed that a cyclobutadiene intermediate had not been formed - "this indicates that a cyclobutane structure plays a part in the reaction mechanism, at least a much less unsaturated ring as was formerly suggested". More recently, Rumanian investigations[68] seemed to suggest a shift back in favour of the cyclobutadiene intermediate by involvement of hydrogen abstraction although this is not in keeping with the general trend of opinion.

The stability of the cyclobutane in the presence of a rhenium oxide disproportionation catalyst was studied[67] and it was found that no reaction was detected until the reaction temperature was raised above 573K. Pettit[69] noticed that

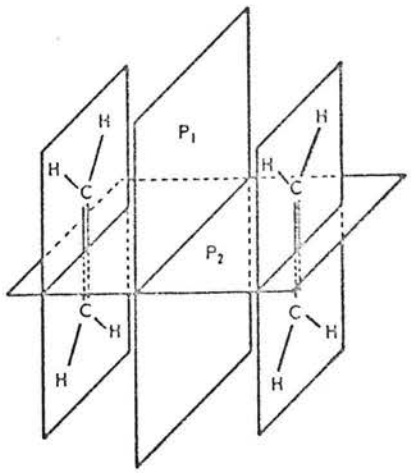
cyclobutane was not formed to any great extent (<0.1%) from ethylene over a molybdena-alumina catalyst and that only 3% ethylene was produced from the reaction of cyclobutane over the same catalyst.

The mechanism of the catalytic disproportionation has been the subject of some theoretical treatment during the last five or six years. It is noticeable that the concerted reaction between the two olefinic double bonds in the cycloaddition is "symmetry-forbidden" according to the rules of orbital symmetry formulated by Woodward and Hoffman[70]. Mango[33,71] has proposed the concerted fusion of two olefin double bonds where "a transition metal system containing d orbitals of sufficient energy and possessing the appropriate number of d electrons can, conceivably, carry out these operations". In describing the fusion of two olefin π-bonds to cyclobutane σ-bonds, the molecular orbitals representing the bonds undergoing character change are combined using the fundamental rules of simple molecular orbital theory. Figs. 2.1, 2.2 and 2.3 give a complete molecular orbital description of the interaction of two olefin π-bonds.

From Fig. 2.2 this orbital crossing is characteristic of a forbidden reaction. As the reaction proceeds, the electron pair in the SSπ combination flows into the cyclobutane SS σ bond, while the electron pair in the ASπ combination moves into the cyclobutane ASσ^* bond. The net bonding between the approaching olefins is, therefore, essentially zero across the reaction co-ordinate.

FIGURE 2.1

Symmetry Elements for π-bond Fusion

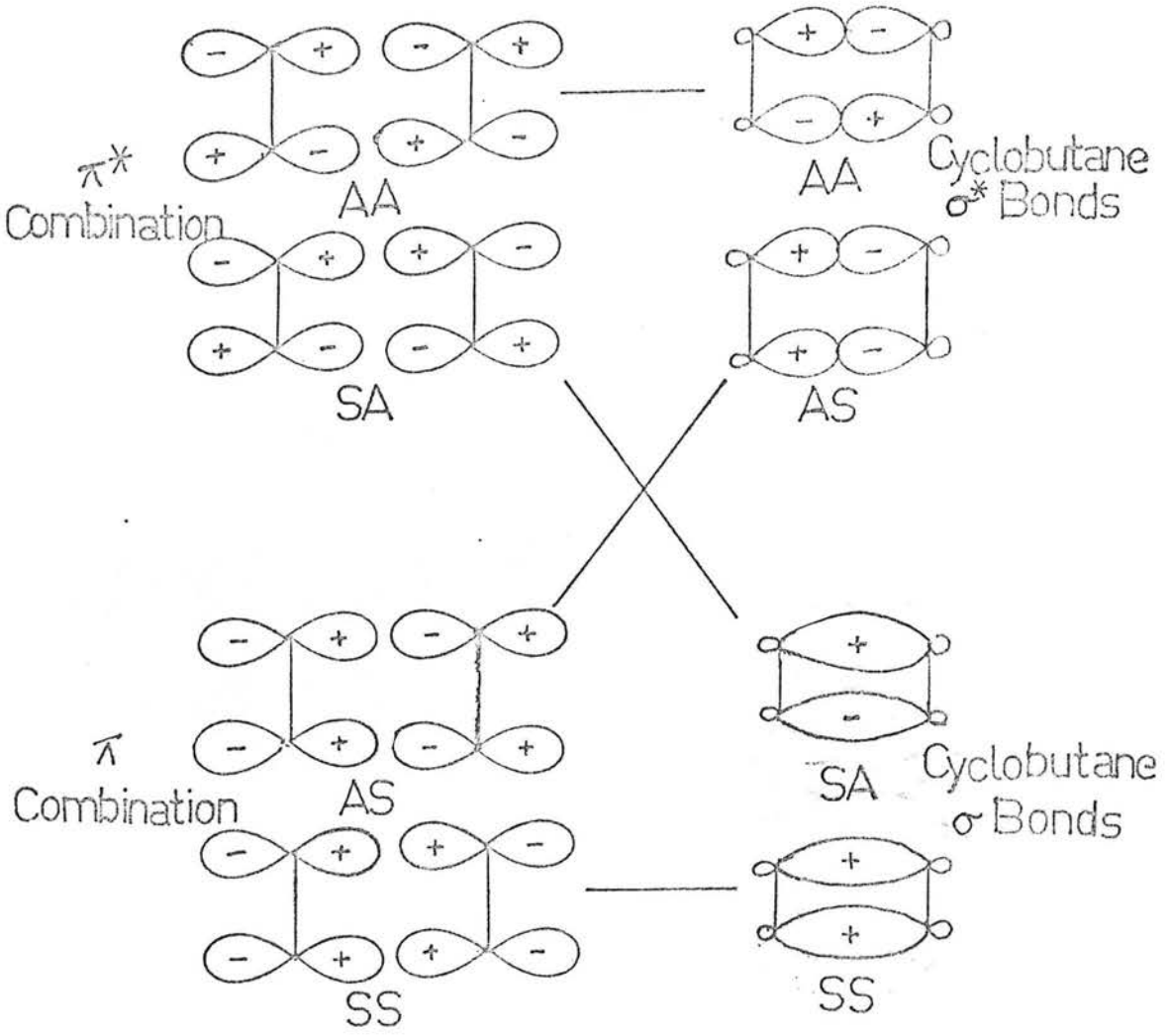


For cyclobutanation, the elements of symmetry are two planes, P_1 and P_2 (Figure 2.1). In Figure 2.2 the assignment SA, for example, means symmetric about P_1, and antisymmetric about P_2.

It is timely to consider the role of an appropriate transition metal in effecting the smooth, ground-state interconversion of two olefins and a cyclobutane ring. The construction of a cyclobutane ring requires the electronic population of its SA and SS orbitals and the electronic vacancy of the AA and AS orbitals. Two of the prerequisites - population of the SS orbital and vacancy of the AA orbital - are assured, since these orbitals are correlated with the appropriate orbitals in the olefin combinations. The catalyst, in the form of a transition metal, is clearly required to remove an electron pair from the olefin AS π combination and subsequently insert an electron pair into the olefin SA π^* combination. Hypothetically, a catalyst can perform these operations by using a pair of orbitals of SA

FIGURE 2.2

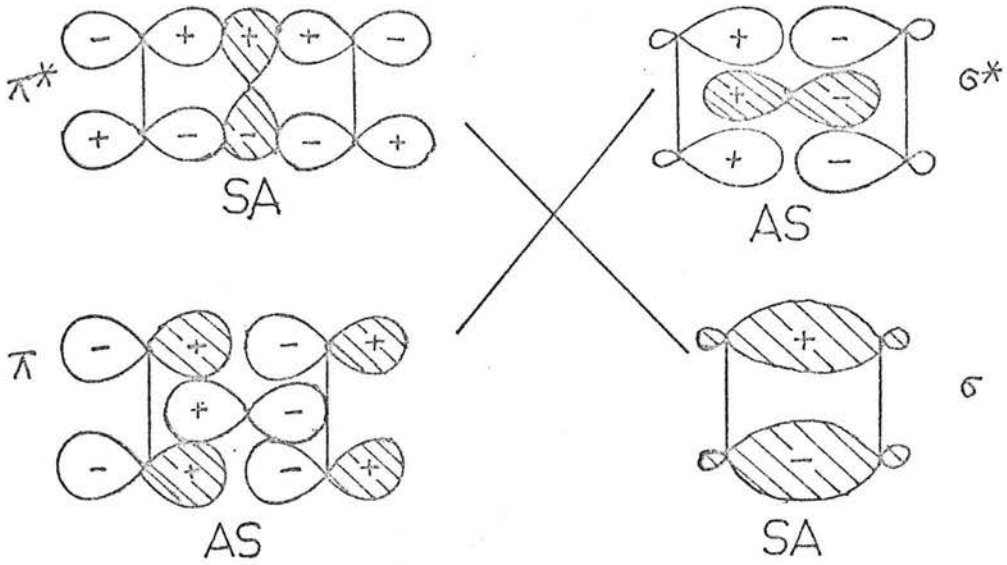
Correlation Diagram for the Interconversion of a Cyclobutane Ring with Two Olefins



and AS symmetry and an electron pair. Fig. 2.3 represents the role of these metal orbitals. For simplicity, the electron pairs have been localized (indicated by shading) in the originating and terminating bonds.

FIGURE 2.3

Correlation Diagram of the SA and AS Orbitals and Orbitals of the Hypothetical Catalyst



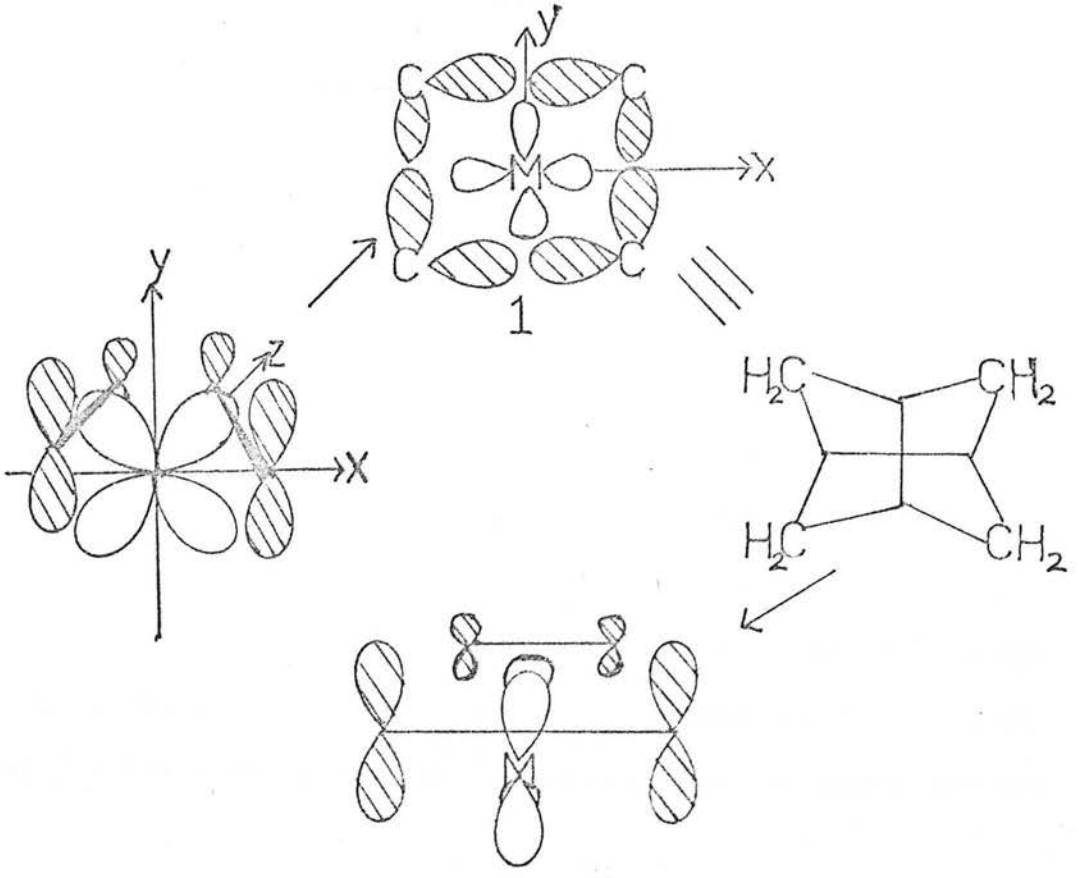
It is perhaps unwise to consider localization of electrons as such. It is probably more accurate to think of an electron pair from the catalyst (i.e. the metal) flowing into the incipient cyclobutane SA σ bond through a catalytic orbital of that symmetry while a pair of electrons from the AS π combination of the transforming olefins flows into a catalyst orbital of that symmetry. In essence, this means that the catalyst in question must have electrons located in an SA orbital and at the same time it must have an empty orbital of the AS symmetry, capable of receiving an electron pair. In the ideal case, it would be

better if the SA and AS catalyst orbitals were of the non-bonding type so that the flow and counterflow of electrons would not disrupt the bonding character of the catalyst.

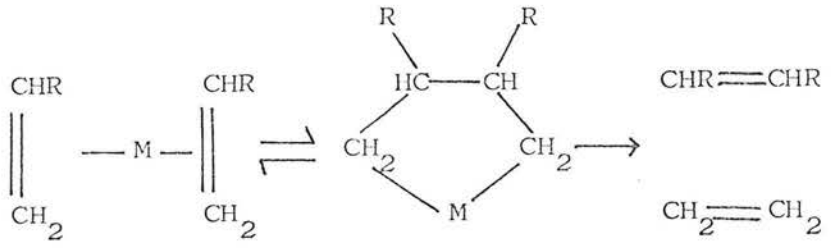
The fact that cyclobutane was so stable over a disproportionation catalyst caused Pettit[69] to propose an alternative orbital pathway to that presented by Mango. Pettit suggested that the four carbon atoms of the intermediate are not to be considered as a cyclobutane ring, but as being composed of four methylenic units. The molecular orbitals of these units interact with the requisite metal orbitals (Figure 2.4) in such a way that the rupture of the carbon-carbon σ bonds of the reacting olefins occur at the same time as π-orbitals of the olefins are transforming so that a cyclobutane molecule is not formed.

FIGURE 2.4

Formation of Disproportionation Products Via the Methylenic Intermediate 1



More recently, there has been some support in favour of a metallocycle type of intermediate (a five-membered ring including the metal atom) and evidence has been provided for such a species[72] in a homogeneous system.



In this case, the metal M was tungsten from a WCl_6:n-BuLi system.

Kinetic studies of the disproportionation reaction have been quite few, but since the discovery of the heterogeneous reaction, two types of mechanism have been proposed. Firstly, the kinetic studies carried out involving the disproportionation of propene over a tungsten oxide on alumina catalyst rendered results[73] which coincided with a Rideal type mechanism, i.e. one molecule of propene adsorbed on the catalyst surface reacting with one molecule of propene in the gas phase. The reaction temperature was between 589 and 728K. Kinetic studies carried out on supported cobalt molybdate indicated[74] that for the disproportionation of propene at lower reaction temperatures (394 - 478K) a Langmuir mechanism was taking place. This involves the reaction of two adsorbed propene molecules on the catalyst surface. These latter recommendations have been endorsed by kinetic studies in a static system of the reaction of propene on a molybdenum hexacarbonyl on alumina catalyst[74]. These kinetic studies [75] showed that both first and second order plots for reversible systems were equally well obeyed, but further investigations[76], using a butene system where

preferential adsorption did not hamper kinetic order calculations, indicated that the reaction rate depended on the second power of propene concentration.

2.6 Object of the Present Investigation

Most of the work published on disproportionation catalysts has concerned the oxides and carbonyls of molybdenum and tungsten. It was intended originally to investigate other metal carbonyls and related complexes as possible sources of active disproportionation catalysts. This study was hindered by the irreproducibility of catalyst activity and, after the development of a more reproducible catalyst preparation technique, it was decided to examine the role of the support in the catalysis.

Although there has been a sizable amount of work published on various catalyst systems for the disproportionation of olefins, the part played by the support in such systems has attracted little attention. The investigation of a molybdenum hexacarbonyl catalyst involved a study of the effect of varying the pretreatment temperature of the oxide support on the initial rate of disproportionation. Variation of the catalyst activation temperature was also studied and, with the aid of spectroscopic techniques, it was possible to clarify the state of the active catalyst.

These findings prompted the study of various organometallic complexes of tungsten and molybdenum supported on silica and alumina. Using the same reproducible technique, the activities of a range of non-carbonyl-containing catalysts were measured.

CHAPTER THREE

EXPERIMENTAL APPARATUS AND TECHNIQUES

3.1 Introduction

The experimental work described in this thesis can be conveniently divided into two main sections:

1. The study of the reaction of propene over various supported organometallic catalysts. This work was carried out in a static vacuum gas handling system, using gas chromatography as the means of analysis. The apparatus and experimental techniques are described in detail later in this chapter (Sections 3.2, 3.3 and 3.4).

2. Spectroscopic techniques. Various methods were employed in an attempt to identify the active catalytic species derived from certain supported molybdenum hexacarbonyl catalysts. This was attempted by using e.s.r. spectroscopy allied to the information obtained from an infrared technique. X-ray fluorescence, atomic absorption spectrophotometry and X-ray diffraction were also techniques employed in this investigation.

3.2 Gas Handling System

Figure 3.1 shows diagramatically the design of the gas handling system which was used for the kinetic study of the disproportionation reaction of propene. The apparatus was constructed throughout from "Pyrex" glass with ground glass joints and stopcocks lubricated with "Apiezon L" or "Apiezon T" vacuum grease. There were two pumping systems, each consisting of an electrically heated mercury diffusion pump with a cold tap backed by a

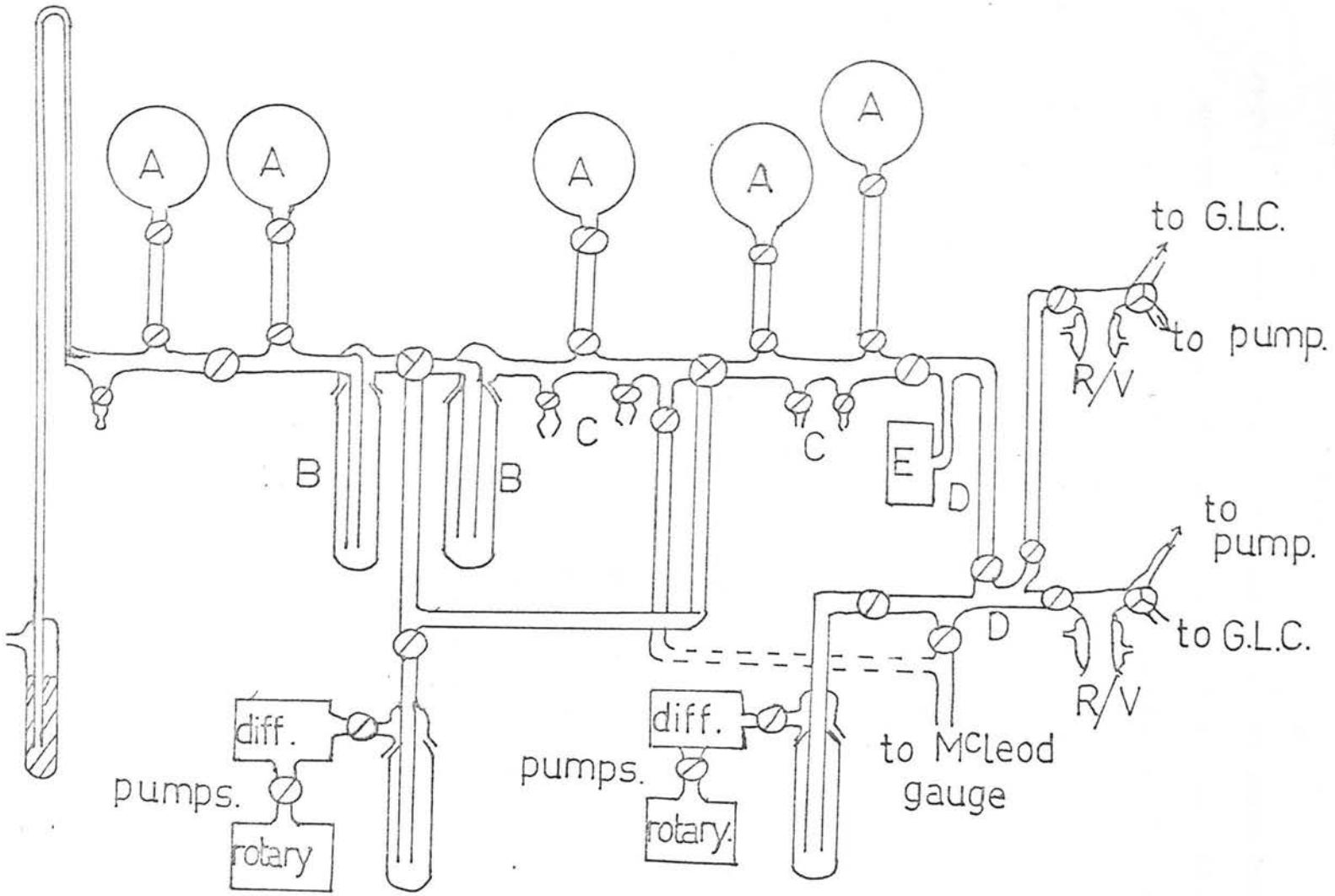


Fig. 3.1. Gas Handling System.

two stage "Speedivac" rotary oil pump. For a period during the experimental work, a Leybold-Heraus oil pump was used instead of one of the "Speedivac" pumps. One set of pumps was used to evacuate the reaction vessels, while the other evacuated the rest of the apparatus. The vacuum at various points of the system could be checked using the McLeod gauge for which a "sticking" pressure was less than $1.33 \times 10^{-4} Nm^{-2}$.

Gases were stored in the bulbs (A) after purification by vacuum distillation in traps (B). Liquids were kept in sample tubes which were attached by ground glass joints at C, and those compounds which might dissolve tap grease were stored under liquid nitrogen.

The section of the gas line, D, was used as the dosing volume for reactants. Pressures were measured using the diaphragm vacuum gauge, E, and in this way mercury was excluded from the dosing volume D and the reaction vessel F. The volumes of D and F were found by expanding air from a measured bulb attached to the apparatus at C. The volumes measured were:

Dosing Volume D = $1.56 \times 10^{-4} m^3$

Reaction Volume F_1 = $2.54 \times 10^{-4} m^3$

Reaction Volume F_2 = $1.66 \times 10^{-4} m^3$

The cylindrical reaction vessel was connected to the apparatus by a water-cooled B24 double O-ring cone and socket joint. Temperature control of the reaction vessel(s) was achieved by use of a furnace or a water bath depending on the temperature required. For temperatures between 298K and 313K the reaction vessel was surrounded by a "Thermos" flask containing water at the particular temperature required. Higher

temperatures were maintained by a close fitting furnace, the temperature of which could be controlled to within ±0.5K by use of a "Variac" voltage controller and a Fielden "Bikini" temperature unit. Temperatures were measured by a chromel-alumel thermocouple.

Samples of the gas mixture in the reaction vessel F could be removed for analysis by gas chromatography. This was done using a three-way tap G, with connections to the reaction vessel, the sampling volume and the pump. It was assumed that the composition of a sample was representative of the composition of the whole reaction mixture at the time of withdrawal, each sample being approximately 2% of the reaction mixture present in the reaction vessel. The valve used to inject the sample into the chromatograph was a Perkin Elmer unit which provided a means of switching a sample loop alternately between the sampling volume and the carrier gas stream.

3.3 Gas Chromatographic Unit and Analysis

A Perkin Elmer type F11 gas chromatograph was used throughout this part of the work. The 4m column of bis-2-methoxy-ethyl adipate (20%) on Chromasorb P, which was found suitable for the type of analysis to be undertaken was mounted in an oven assembly capable of temperature control of ±0.1K. A flame ionisation detector was used with nitrogen as the carrier gas, and the amplified signals from the detector went to a Kent "Chromalog 3" Digital Integrator and a Goerz "Servoscribe" recorder.

Optimum analysis of C_2 to C_6 olefins which represented typical disproportionation reaction mixtures was obtained by adjusting the operating conditions of the gas chromatograph unit.

The optimum pressures of the gases, which were controlled by reducing heads on the cylinders followed by pressure control valves on the connecting tubing, were found to be:

Nitrogen	210 kNm^{-2}
Hydrogen	120 kNm^{-2}
Air	170 kNm^{-2}

The optimum column temperature was 303K.

With these operating conditions separation and analysis of ethylene, propane, propene, but-1-ene, trans-but-2-ene, cis-but-2-ene, pentenes and hexenes was possible. The column was calibrated for various hydrocarbons by measuring their retention times and its relative sensitivity to them. The latter calibration was achieved by analysing prepared mixtures of the hydrocarbons and calculating the factors correlating the peak areas measured by the integrator and the known pressures of the components of the gas mixture. These sensitivity factors were checked on several occasions during the period of research.

3.4 Materials

Supports

All the supports were calcined at 923K for 18h before use. Details of the supports appear in Table 3.1. Surface area measurements after calcination were determined by adsorption of nitrogen at 77K.

Organometallic Catalysts

Table 3.2 contains the organometallic catalysts which were tested for activity in propene disproportionation. The method

of preparation of the supported catalyst is also included. Most of the organometallic compounds were synthesized within this Department, except for the carbonyls of molybdenum, rhenium and manganese, which were provided by B.D.H. Ltd.

Sodium and lithium halides were Analar grade chemicals.

Gaseous Reactants

(Ethylene, propene, but-1-ene, cis- and trans-but-2-ene, acetylene: Matheson. C.P. Grade and 3,3,3-trifluoropropene, Fluorochem. Ltd.) Each compound was degassed and distilled under vacuum before use, the middle third being retained. The level of impurities was less that 0.1% except for propene which contained propane to an extent of not more than 3%.

Liquid Reactants

(Cis- and trans-pent-2-ene; cis- and trans-hex-2-ene; chlorinated olefins.) These compounds were degassed by repeating a cycle of freezing, pumping and thawing several times. Liquid reactants were stored under liquid nitrogen to prevent contamination by tap grease.

* The author wishes to acknowledge the valuable assistance of Dr. Eric Wharton, Dr. Walter Mowat and Mr. Steven Henderson in preparing the organometallic complexes.

TABLE 3.1

Support	Source	Surface Area ($\times 10^5 m^2 kg^{-1}$)
γ-Al_2O_3	Peter Spence (A)	1.81
SiO_2	Fischer (923)	4.71
MgO	Ramsey[77]	0.49
SiO_2-Al_2O_3	I.C.I.Ltd. (45% Al_2O_3)	2.08
Sugar Charcoal	B.D.H.Ltd.	0.64
Na 13X zeolite	Linde	9.00
$NH_4^{III}X$ zeolite	Coutts[78]	9.00

TABLE 3.2

Compound	Support	Preparation
$Mo(CO)_6$	γ-Al_2O_3	1,2,3
$Mo(CO)_6$	MgO, SiO_2-Al_2O_3, SiO_2, C	1
$Re_2(CO)_{10}$	γ-Al_2O_3	1,2,3
	SiO_2	1
$Cr(CO)_6$	γ-Al_2O_3	2
$Fe_2(CO)_9$	γ-Al_2O_3	3
$Mn_2(CO)_{10}$	γ-Al_2O_3	2
Mo(cycloheptatriene)$(CO)_3$	γ-Al_2O_3	2,3
$[$Mo(cyclopentadiene)$(CO)_3]_2$	γ-Al_2O_3	2,3
Mo(norbornadiene)$(CO)_4$	γ-Al_2O_3	2
$(Ph)_3P$ $Mo(CO)_5$	γ-Al_2O_3	2
$Mo(CO)_5I$ NMePy *	γ-Al_2O_3	2
$(CCl_2{=}CHCl)Mo(CO)_5$ ‡	γ-Al_2O_3	2
Mo(mesitylene)$(CO)_3$	γ-Al_2O_3	1,2
Mo(toluene)$(CO)_3$	γ-Al_2O_3	1,2
Mo(p-xylene)$(CO)_3$	γ-Al_2O_3	1,2
PH_3 $Mo(CO)_5$	γ-Al_2O_3	2
Mo_2(acetate)$_4$	γ-Al_2O_3	3
$MoCl_5$	γ-Al_2O_3	3
$Mo_2(CH_2SiMe_3)_6$	γ-Al_2O_3, SiO_2	1
$Mo_2(CH_2CME_3)_6$	γ-$Al_{2,3}$, SiO_2	1
$W(CH_3)_6$	γ-Al_2O_3, SiO_2, charcoal	1
$W_2(CH_2SiMe_3)_6$	γ-Al_2O_3, SiO_2	1
$W_2(CH_2CMe_3)_6$	γ-Al_2O_3, SiO_2	1
$W(ONMeO)_2(CH_3)_4$	SiO_2	1

TABLE 3.2 (continued)

$Re(CO)_5Br$	γ-Al_2O_3	2
$Mn(CO)_5Br$	γ-Al_2O_3	2
Cr(cycloheptatriene)$(CO)_3$	γ-Al_2O_3	2

---

* N-methyl pyridinium ion

‡ Compound of uncertain nature

Preparation 1: impregnation "in situ"

Preparation 2: impregnation "in air"

Preparation 3: dry-mixing

3.5 Catalyst Preparation

Most of the catalysts which were tested in the course of this work were prepared by an "in situ" method of impregnation, in which the support pretreatment and the impregnation process were both carried out *in vacuo*. The reaction vessel which was used in the preparation is described in Figure 3.2.

Catalyst samples were prepared in the silica reaction vessel attached to the gas line as indicated in Section 3.2. The catalyst support (usually 10^{-4}kg) rested at the bottom of this reaction vessel ($2.54 \times 10^{-4} m^3$) and was outgassed *in vacuo* at the desired temperature for 1h, cooled to room temperature and about 20kNm^{-2} of dry oxygen-free nitrogen admitted. A degassed solution of the organometallic compound in a suitable hydrocarbon solvent under nitrogen was then slowly run on to the support through a greaseless stopcock at the top of the reaction vessel, and allowed to remain in contact with the support for a period of at least 45 minutes. The solution was sufficient to give a 10% by weight organometallic compound to support ratio. The solvent and any excess organometallic were then removed by careful pumping, and the catalyst activated at the desired temperature *in vacuo*. The prior admission of nitrogen was necessary to avoid deposition of the organometallic compound on the walls of the reaction vessel. The solvent, which was normally sodium-dried cyclohexane, was distilled under nitrogen over calcium hydride and stored over 4A Linde molecular sieve.

Although this was the method most widely used in this work, it was only developed after measuring the activities of several catalysts using the method of impregnation which involved

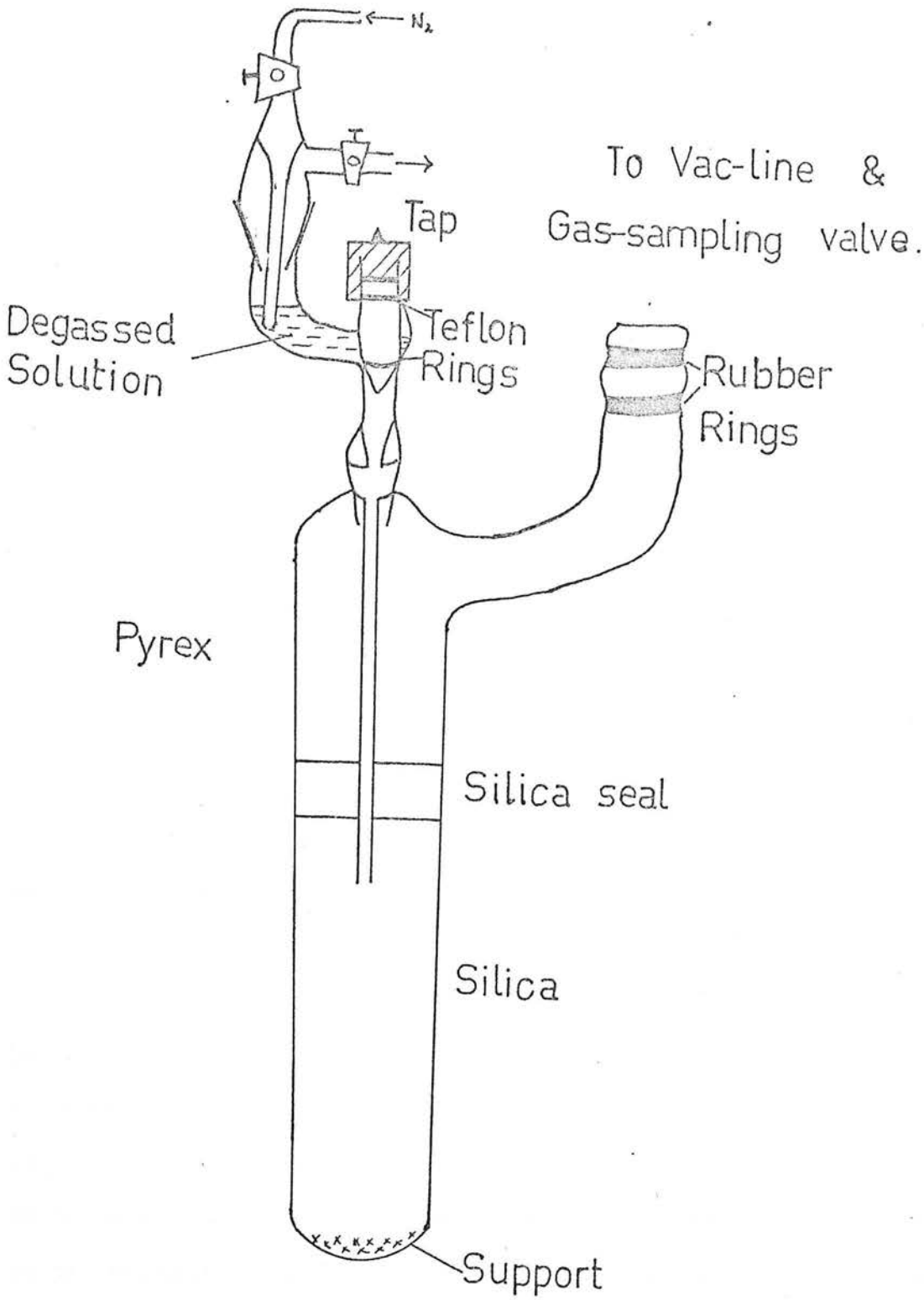


Fig. 3.2. "In situ" Reaction Vessel.

pretreating the support in air and impregnating under the same conditions. The development of the "in situ" type of preparation is described in Chapter 4. Dry-mix catalysts were also tested, whereby the organometallic compound was ground with the support in a mortar until a fine powder was achieved. Again, appropriate proportions of each component were used to prepare catalysts of the required nominal compositions. In the case of both these types of preparation, the alumina support was heated in air at 673K before impregnation or dry-mixing, and the reaction vessel used had a volume of $1.66 \times 10^{-4} m^3$.

3.6 Spectroscopic Techniques

E.s.r. spectra were recorded on a Decca X-1 spectrometer, operating at 9.27 GHz with 100 KHz magnetic field modulation. Catalysts were treated in a pyrex reaction vessel fitted with a stopcock and a 4 m.m. o.d. quartz side arm. After treatment on a conventional gas handling line, the catalyst could be transferred under vacuum to the side arm for recording spectra. Infrared spectra were recorded on a Perkin Elmer 225 infrared spectrophotometer. Catalyst samples for most of the work were in the form of pressed discs and weighed 30 mg. These discs were mounted in a brass sample holder centred in a cylindrical pyrex cell with potassium bromide windows. The infrared cell was connected to a gas handling vacuum line and catalyst activities could be determined by exposing the sample to a pressure of propene and any products were trapped out at 77K and analysed by gas chromatography. For several infrared experiments in the early part of the work described in this thesis (Chapter 4) the spectra of air-sensitive catalyst samples were investigated by

sealing the active samples under vacuum, breaking the seal and preparing a Nujol mull in a glove bag filled with nitrogen. An air tight cell specially designed to accommodate the infrared plates was used to prevent the access of air while the spectra were being run. Again the Perkin Elmer 225 infrared spectrophotometer was used to record spectra.

Analyses for the molybdenum content of various catalysts were carried out by atomic absorption and X-ray fluorescence. In the analysis for molybdenum by atomic absorption, a Varian Techtron A4 spectrometer was used on samples which were dissolved in aqueous acid. The analyses determined by X-ray fluorescence were carried out at I.C.I.(Ltd.). The X-ray diffraction pattern of a powdered catalyst sample was measured using a Philips powder diffractometer.

* The author would like to thank Mr. Graham Derby for the molybdenum analyses by atomic absorption, Dr. R.O. Gould for the X-ray diffraction measurements and I.C.I.(Ltd.) Agricultural Division for the molybdenum analyses by X-ray fluorescence.

CHAPTER FOUR

THE DEVELOPMENT OF THE PREPARATIVE TECHNIQUES FOR DISPROPORTIONATION CATALYSTS

4.1 Introduction

Supported molybdenum hexacarbonyl has been the most widely used transition metal catalyst in the disproportionation of olefins[4,38,75]. Little work has been carried out on other transition metal carbonyls. Initially this investigation was directed towards discovering other carbonyl catalysts which were active for propene disproportionation. Transition metal carbonyls other than molybdenum hexacarbonyl were tested for activity. The effect of added lithium salts to the supported molybdenum hexacarbonyl catalyst was also investigated.

These catalyst samples were prepared either by impregnation or by a dry-mixing technique and it was found that it was virtually impossible to reproduce any trend in activity with either technique. In this chapter, the development of a reproducible system is described using molybdenum hexacarbonyl supported on γ-alumina prepared by an "in situ" technique. A more active catalyst is obtained by this technique than by the impregnation or dry-mixing methods described earlier.

Using this technique, the effect of halogenated olefins on the activity of the supported molybdenum hexacarbonyl catalyst was investigated. As reported previously[51], the activity of the catalyst was promoted as a result of this treatment.

4.2 Experimental

The experimental work in this investigation is concerned mainly with the preparative techniques of the various catalysts. The impregnation and dry-mixing techniques have been detailed in Chapter 3 together with the "in situ" method of catalyst preparation. Development of the latter technique will be described in this chapter. In the case of the added lithium halide work, the alumina support, which had been pretreated at 673K for 1h in air, was ground with the requisite proportion of lithium halide and molybdenum hexacarbonyl until a fine powder was achieved. Unless otherwise stated, the catalyst sample (5×10^{-4}kg) was in all cases 5% by weight of catalyst to support, and for catalysts prepared by impregnation the solvent used was benzene or cyclohexane.

The apparatus and experimental technique for this work was described in Chapter 3. The measurements of catalyst activity were determined from the initial rate of disappearance of propene. Unless otherwise stated, the measurement of catalyst activity was obtained from the reaction of 1.06kNm^{-2} of propene at 298K.

The infrared technique employed in this work is described in Chapter 3. The relevant metal-carbonyl stretching frequencies were observed in the infrared region between 1800 and 2100cm^{-1}, and carbon-carbon double bond stretching frequencies in the region 1500 to 1700 cm^{-1}.

4.3 Results

4.3.1 Transition Metal Carbonyl Catalysts Other Than Molybdenum

$Re_2(CO)_{10}$ supported on γ-Al_2O_3

This catalyst was tested for activity in propene disproportionation and, although several batches of the catalyst were prepared by impregnation, there was no visible sign of products. A catalyst sample was also heated to 543K and, although no disproportionation was detected, a film of rhenium metal was deposited on the inner walls of the reaction vessel. The reaction temperature was raised to 333K on two occasions to remove any possible adsorbed species and no products were observed.

The patent work of Williams and Turner[47] indicated that pretreatment of the alumina support with mineral acid was necessary in producing an active rhenium carbonyl catalyst. In this pretreatment, 0.1N hydrochloric acid was allowed to run through a column of γ-alumina pellets until the pH of the eluent reached 5.5. A batch of catalyst was prepared in accordance with this publication but no activity of the catalyst was observed. A dry-mix catalyst was also prepared but again no activity was observed. Infrared evidence revealed that there was no loss of carbonyl stretching frequencies at the end of the reaction.

$Re_2(CO)_{10}$ supported on SiO_2

Using the "in situ" method described in Chapter 3, a rhenium

carbonyl catalyst (10^{-4}kg) was prepared by supporting rhenium carbonyl on a silica gel which had been pretreated at 298K for 1h (discussed more fully in Chapter 5). The catalyst was found to exhibit an initial rate of propene disproportionation measured as 0.01% min^{-1}.

$Re(CO)_5Br$ supported on γ-Al_2O_3

Batches of this catalyst were prepared by impregnation using both Spence A alumina and the acid-treated alumina employed in the preparation of the rhenium carbonyl catalyst. In both cases, the catalyst was inactive for propene disproportionation even after activation at 423K.

$Mn_2(CO)_{10}$ supported on γ-Al_2O_3

Catalyst samples were prepared by impregnation using (i) Spence A alumina and (ii) the acid-treated alumina described above. These samples were not found to be active for propene disproportionation. Infrared spectra indicated full retention of the terminal carbonyl stretching frequencies.

$Mn(CO)_5Br$ supported on γ-Al_2O_3

A catalyst sample was prepared by impregnation and activated at 333K. Reactions were studied at 298K and 333K but no disproportionation was observed.

$Cr(CO)_6$ supported on γ-Al_2O_3

A catalyst sample which had been prepared by impregnation

was activated at 343K and 373K and was found to be inactive at reaction temperatures of 298K, 328K and 343K.

Cr(cycloheptatriene) tricarbonyl supported on γ-Al_2O_3

A catalyst sample, which had been prepared by dry-mixing, was activated at 358K and no activity was observed.

$Fe_2(CO)_9$ supported on γ-Al_2O_3

A dry-mixed catalyst sample showed no activity for propene disproportionation after activation at 373K and 423K.

4.3.2 Preparation of 5% $Mo(CO)_6$ on γ-Al_2O_3

Preparation	Initial Rate/ ($\%\ min^{-1}$)
Dry-mix	0.42
Impregnation (hexafluorobenzene)	0.70
Impregnation (trichloroethylene)	0.34

All samples were activated at 373K before reaction with 1.06kNm^{-2} of propene.

4.3.3 Effect of Added Lithium Halides

These alumina supported catalysts (5% $Mo(CO)_6$ to support by weight) were prepared by dry-mixing the added salt with the powdered molybdenum hexacarbonyl catalyst. The weight of added halide was varied to produce catalysts with a range of Li:Mo molar ratios. All samples were activated at 373K for 1h and a dose of propene sufficient to give a pressure of 1.06kNm^{-2} in

TABLE 4.1

Catalyst (on γ-Al_2O_3)	Molar Ratio	Initial Rate/ (% min^{-1})
$LiF:Mo(CO)_6$	1:1	0.62
	3:1	0.44
	5:1	0.17
	6:1	1.84, 0.32, 0.80, 0.08
	10:1	0.48
$LiCl:Mo(CO)_6$	1:1	0.46
	6:1	1.90
	12:1	0.90
$LiI:Mo(CO)_6$	1:2	1.78
	1:1	0.31
	6:1	0.07
$NaF:Mo(CO)_6$	6:1	0.20, 0.46
5% $Mo(CO)_6$	-	0.42

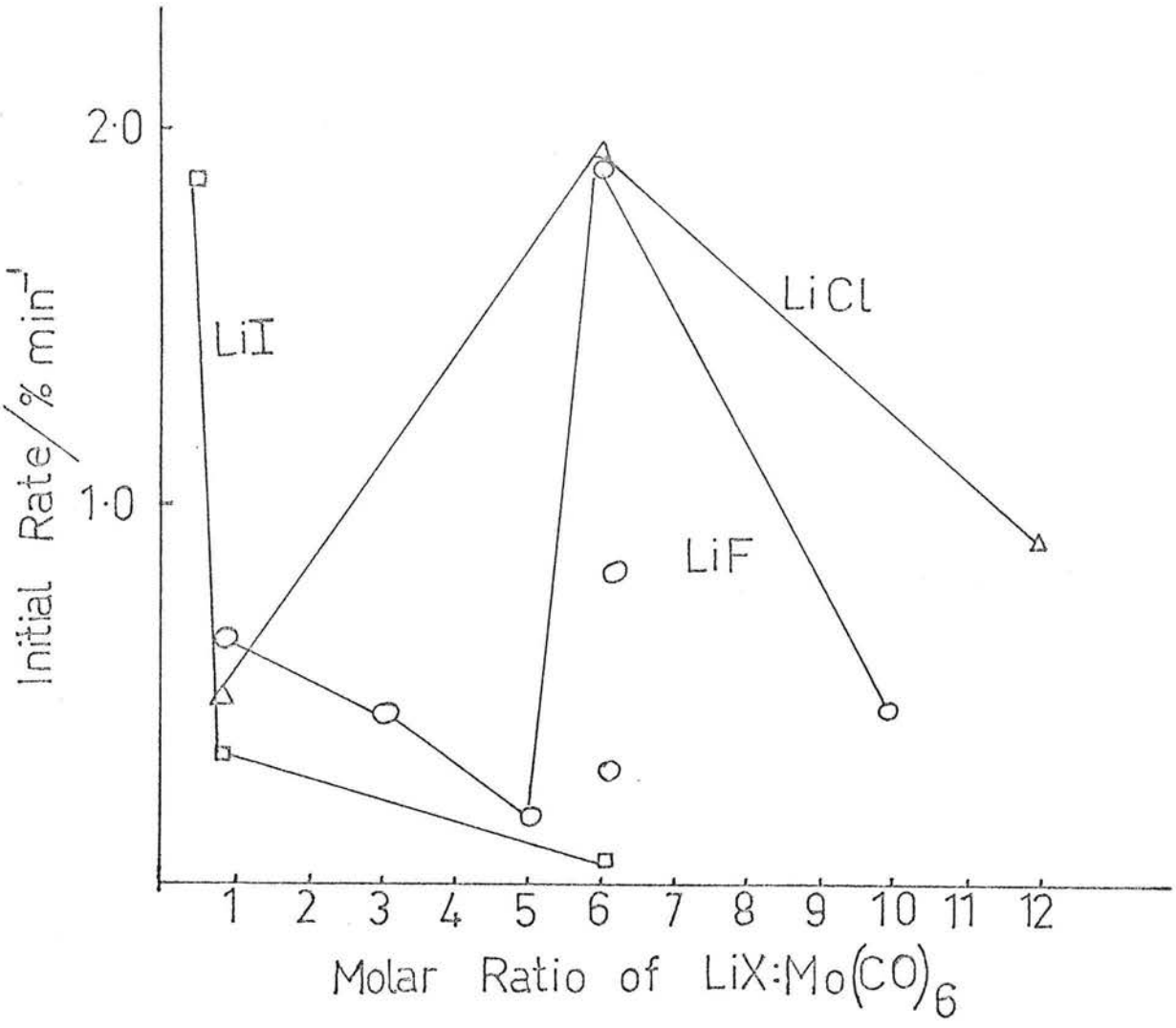


Fig. 4.1. Effect of added Lithium Halides.

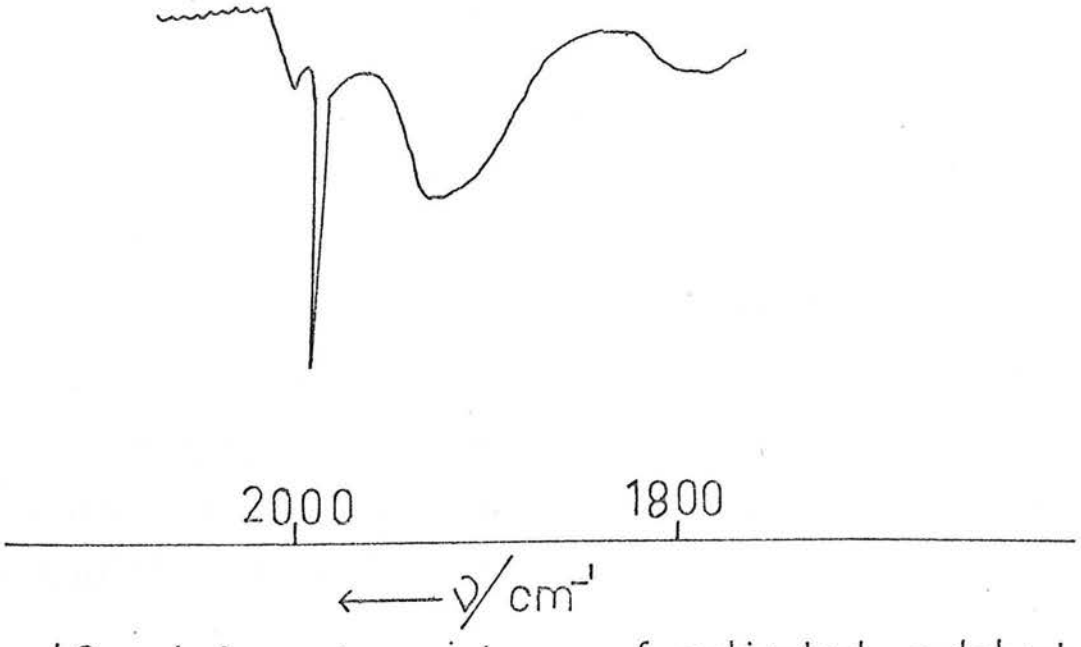


Fig. 4.2. Infrared spectrum of activated catalyst.

the reaction vessel (F_2) was allowed to contact the catalyst. Sodium fluoride was also tested.

Table 4.1 contains the results of the investigation in the form of initial rates of propene disproportionation for each of the catalyst samples. Figure 4.1 demonstrates the trends graphically. Two of the catalyst samples were prepared again and tested for reproducible results (Table 4.1). Figure 4.2 shows the infrared spectra for an activated catalyst of the type $LiF:Mo(CO)_6$ = 6:1. The Nujol mull was prepared under an atmosphere of nitrogen.

4.3.4 Study of the $Mo(CO)_6/Al_2O_3$ System: Reproducibility of Results

The irreproducibility of the lithium halide/molybdenum hexacarbonyl system necessitated an investigation into the method of preparation of $Mo(CO)_6$ catalyst samples. An attempt was made to control certain variables which rendered such samples incapable of reproducing catalyst activities.

Preparation of Catalyst Samples Under Nitrogen

Three separate catalyst samples were prepared as follows. The alumina support, 5×10^{-4}kg was activated at 673K, cooled and impregnated under an atmosphere of nitrogen. The reaction vessel containing the catalyst was connected to the gas line with minimum contact with the atmosphere and the catalyst sample activated *in vacuo* at 373K for 1h. The initial rates of disproportionation for the three similarly prepared samples were 0.8% min^{-1}, 0.4% min^{-1} and 0.2% min^{-1}.

The reaction vessel (F_1) used in this technique is described in Chapter 3. Initially 5×10^{-4}kg samples of the alumina support were used and the initial rates of disproportionation were much faster than the previous impregnation method. In this series of experiments a pressure of $1.33 kNm^{-2}$ of propene was admitted to the reaction vessel. These results are contained in Table 4.2. It was noticed that this technique, using alumina supported molybdenum hexacarbonyl catalysts, produced a more active catalyst than that observed during the extensive study of the alumina supported molybdenum hexacarbonyl system.[76] Initial rates of disproportionation from this latter work are also presented in Table 4.2. The samples were 5% $Mo(CO)_6/Al_2O_3$ and the activity was measured from the initial rate of disproportionation of $1.06 kNm^{-2}$ propene at 298K. The period of evacuation between runs was between 2h and 48h. Temperature of evacuation was 298K. These initial rates, assigned to the new "in situ" technique, were examined from first and second order reversible rate equations of the type:

$$\ln(x_o - x_e) - \ln(x_t - x_e) = \frac{k_1 t x_o}{(x_o - x_e)} \qquad (1)$$

and

$$\frac{\ln(x_o - x_t)(2x_e - x_o) + x_o(x_o - x_e)}{x_o(x_t - x_e)} = \frac{2k_2 t x_o x_o}{(x_o - x_e)} \qquad (2)$$

Where x_o = initial propene concentration, at time t = 0

x_e = equilibrium propene concentration

x_t = propene concentration at time t

k_1 = first order rate constant

k_2 = second order rate constant

TABLE 4.2

Run	Sample A		Sample B		‡
	1st Order	2nd Order	1st Order	2nd Order	
1	-	-	0.9	0.9	.08
2	4.1	4.0	4.8	4.5	.46
3	15.6	19.8	10.1	7.2	.46
4	10.6	8.3	3.4	3.2	.46
5	9.9	9.7	4.8	4.4	.43
6	-	-	3.3	3.1	.47

‡ Initial Rate/(% min^{-1})(76)

Catalyst Colour Changes

Although the γ-alumina was white after pretreatment at 673K, the catalyst took on a pale yellow colour after impregnation of the solution of the hexacarbonyl and evacuation at 298K. After activation of the catalyst at 373K, it normally changed colour to light grey.

4.3.5 Alumina Pretreatment of the $Mo(CO)_6/Al_2O_3$ Catalyst

Using the "in situ" preparation, which afforded a more active catalyst, a study was made of the pretreatment temperature of alumina in the range of 473K - 773K. After impregnation for 45 mins, all samples were activated at 373K for 1h. The results of the alumina pretreatment are presented fully in Chapter 5 but are relevant here in that a favourable degree of reproducibility of catalyst activity was obtained. As a result of the extremely fast initial rates observed with this preparation (Table 4.2), the weight of catalyst sample was reduced to 10^{-4}kg. A pressure of propene corresponding to 3.33kNm^{-2} was admitted to the reaction vessel. Table 4.3 demonstrates the degree of reproducibility achieved.

Table 4.3

Temp. of Pretreatment/K	Initial Rate/(% min^{-1})
473K	0.29
573K	1.02, 0.78
673K	0.71, 0.82
773K	0.63, 0.61

Samples prepared by this method did not always have their activities enhanced by evacuation at 313K after the first run. Although this was consistently detected in the work reported by Davie[76], an increase in activity was not guaranteed from the "in situ" technique.

A sample of alumina was outgassed at 573K for 16h and a catalyst prepared and activated in the same way. An initial

rate of disproportionation of 0.40% min^{-1} was measured. A sample of catalyst was also prepared by impregnating the solution of molybdenum hexacarbonyl for 11h on alumina pretreated at 573K for 1h. An initial rate of 0.34% min^{-1} was measured.

4.3.6 Effect of Halogenated Olefins on the Initial Rate of Disproportionation

After a similar study[51] using the $Mo(CO)_6/\gamma\text{-}Al_2O_3$ catalyst, it was decided to investigate the effect of such activity promoters using a more active catalyst prepared by the "in situ" technique. Each catalyst sample underwent the same preparative and activation procedure. Using a 10^{-4}kg sample of alumina pretreated at 573K for 1h, a 10% by weight catalyst was prepared as described in Chapter 3. The sample was activated at 373K for 1h and, after cooling to 298K, it was exposed to 3.33kNm^{-2} for 1h, evacuated at 313K for 2h, exposed to 3.33kNm^{-2} of propene at 298K, the initial rate measured, and the sample evacuated again at 313K for 2h. Then the catalyst was exposed to 3.33kNm^{-2} of the halogenated olefin for 1h at 298K and, after evacuation at 313K for 2h, the activity of the catalyst was measured at 298K, using a pressure of 3.33kNm^{-2} of propene. The degree of enhancement was calculated by comparing the two initial rates measured before and after the exposure to the halogenated olefin. The results of this investigation are contained in Table 4.4. No disproportionation of the halogenated olefins was detected. Results obtained by Davie also appear in Table 4.4.

TABLE 4.4

Promoter	Initial Rate/(% min^{-1})		Increase	Increase
	Before Treatment	After Treatment	Factor	Factor[51]*
3,3,3-trifluoropropene	0.35	3.05	8.7	80
	0.40	2.50	6.3	
trichloroethylene	0.38	2.55	6.7	155
chloroethylene	1.0	2.70	2.7	1
trans-1,2-dichloroethylene	0.72	2.75	3.8	37
3,3,3-trifluoropropene‡	0.01	0.08	8	
	0.03	0.31	10	

‡ For these samples, the γ-Al_2O_3 support was pretreated at 298K for 1h before impregnation.

* Results obtained by Davie et al.[51]

4.4 Discussion

The results obtained from the transition metal carbonyl catalysts can be explained by examining the chemistry of the various triads in the transition element series. The catalysts under investigation were contained in the following triads:

Cr	Mn	Fe
Mo	Te	Ru
W	Re	Os

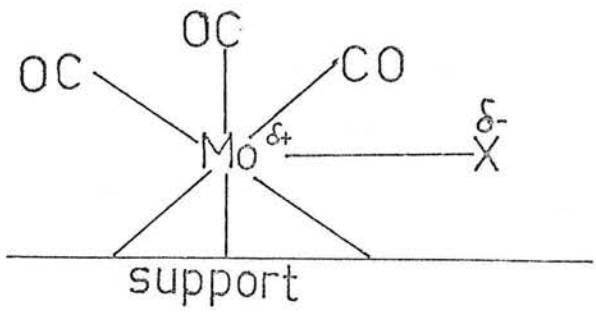
From the chromium triad it is well known that the oxides and carbonyls of molybdenum and tungsten are active disproportionation catalysts when supported on alumina[4,38,47,75]. It would be feasible in the light of this information to expect supported chromium hexacarbonyl to be similarly active. The results from the chromium hexacarbonyl and the cycloheptatriene chromium tricarbonyl, both supported on alumina, indicate that under these conditions of activation, neither catalyst is active for propene disproportionation. Generally, it is thought that the active catalytic site is capable of bringing together the two combining olefins for reaction in such a way that it is reasonable to expect the metal atom to be coordinatively higher than six, bearing in mind interaction of the metal with the support. It is known that molybdenum and tungsten form complexes with coordination numbers higher than six, e.g. $Mo(CN)_8^{4-}$. In the case of chromium complexes, a coordination number higher than six is not well known. Ugo[57] has mentioned a homogeneous chromium arene complex as active for disproportionation, but this work remains unpublished.

The inactivity of the manganese carbonyl catalyst may be explained in a similar manner. Again, although the chemistry of the elements in the manganese triad is quite similar, it may be proposed that manganese is not known to form complexes of coordination number higher than six, which appears to be necessary for the catalytic reaction to proceed. The results obtained in this work from the rhenium carbonyl catalysts supported on alumina seem to indicate inactivity for disproportionation, although the oxide[38] and carbonyl[47] of rhenium have been reported as active. The treatment of the alumina appears to be important if an active catalyst is to be generated. The patent work[47] has indicated that acid treatment of the alumina is necessary. Acid-treated alumina was used in the study of the catalyst in this thesis but no activity was detected. The effect of the treatment by the mineral acid has not been explained by those workers. Infrared studies of supported molybdenum hexacarbonyl[79,80] indicated that a change in the carbonyl spectrum was noticed in the formation of the active catalyst. This change was apparently not detected for the alumina supported rhenium and manganese carbonyl catalysts tested in this work.

The inability of the iron carbonyl to form an active catalyst may be similarly explained. Since it is a first row element in the transition series, it is unlikely to form a species of coordination number higher than six. Mango[81] appeared to believe that iron in a zerovalent oxidation state had the electronic and molecular orbital qualities for activity in the disproportionation reaction. However it is not

certain that the metal would exist as Fe(O) in the active species.

The results obtained from the lithium halide - molybdenum hexacarbonyl catalysts highlighted the poor degree of reproducibility afforded by the dry-mixing technique. The initial rates of disproportionation are comparable with those observed for the $Mo(CO)_6$ on Al_2O_3 system itself, although in the case of each of the three added salts, there appeared to be a maximum activity at a certain molar ratio of halide:carbonyl which produced a catalyst of greater activity than at the other molar ratios. It was thought that the addition of halide to the carbonyl catalyst would allow the generation of a more active catalyst by interaction of the halide(X) with the molybdenum metal and possibly an acceleration in the breakdown to the active species by an electron-withdrawing effect:



The number of carbonyl ligands left attached to the metal in the supported catalyst is not accurately known, but the effect of the halide would be to withdraw electrons from the metal centre thus weakening the molybdenum-carbon bonds of the carbonyl ligands.

An alternative explanation for enhanced catalytic activity by ligand influence is shown by the effect of adding titanium in the form of $Ti(OC_4H_9)_4$ to the molybdenum hexacarbonyl catalyst supported on γ-alumina[82]. These workers noticed that the activity of the catalysts for propene disproportionation was greater if the titanium was present. The enhancement was explained by proposing that the titanium was donating electrons to the molybdenum centre via an oxygen bond and this increase in electron density at the "active" centre was responsible for a more rapid rate of desorption of the olefins formed by the disproportionation process. They cited the desorption of olefins as being the rate-determining step in the reaction scheme. This was not the rate-determining step proposed by other workers[76,83].

The results initially obtained seemed to suggest that for a molar ratio of 6:1 for LiCl and LiF to $Mo(CO)_6$ and 1:2 for LiI to $Mo(CO)_6$ there was in each case a maximum in activity. It is difficult to explain the significance of these molar ratios other than suggest that with the ionic radius of iodide ion greater than the fluoride and chloride, less lithium iodide was required to produce a similar effect to that of the other halides. The failure of the system to reproduce the activities on repeating the experiments obviously limits any definite explanation of the effects observed. Infrared evidence suggests that, for the supported $LiF/Mo(CO)_6$ system which had been activated, there had been some interaction of the fluoride to give a spectrum with three carbonyl bands similar to that obtained from a $Mo(CO)_6/Al_2O_3$ catalyst treated with fluorinated

olefin[51]. A catalyst treated in this way showed enhanced activity and interaction of the fluoride was proposed - shown by infrared spectroscopy. The infrared spectrum of an activated $Mo(CO)_6/Al_2O_3$ catalyst[79] indicated only two carbonyl bonds.

The poor reproducibility of data did not allow further investigation and an attempt was made to remedy this shortcoming by preparing $Mo(CO)_6/Al_2O_3$ samples under nitrogen. However the results obtained only served to indicate that a totally "in situ" preparation was necessary for the reproducibility of catalyst activity.

The development of the "in situ" technique was an advancement in the preparation of catalyst samples in that a system had been devised whereby the activities of catalysts could be compared due to the good degree of reproducibility derived from this method. The data first obtained from catalyst samples prepared by this method immediately indicated that the activity of a sample was greater than that obtained by a dry-mixing or ordinary impregnation technique. The higher activities can be attributed to the presence, in this preparation, of a "cleaner" alumina. Whereas alumina would readsorb water from the atmosphere if activated at 673K and cooled in air, the conditions of alumina pretreatment for the "in situ" technique do not allow this to happen. As a result, a more active "drier" alumina is used for the impregnation step. A more precise study of the outgassing pretreatment of alumina is described in Chapter 5. The fast initial rates of reaction indicated that further investigation would demand a smaller sample of catalyst and the use of standard operating conditions.

The initial rates obtained from these modified conditions indicate a reasonable degree of reproducibility obtainable by this technique. It is noticed that for first run experiments on these catalyst samples, of alumina pretreatment of 5-673K for equivalent weights of catalyst, the activity is 50 to 100-fold greater than from a typical sample prepared by the old impregnation method[76]. The degree of reproducibility approached by that method of impregnation does not allow too precise a comparison.

It can be seen that increasing the outgassing pretreatment period for alumina has no activity-enhancing effect. Similarly a catalyst prepared after an impregnation contact period of 11h does not show any increase in activity. This conclusion can be drawn due to the improved reproducibility of results.

The results obtained from the effect of the halogenated olefins confirm the work carried out by Davie et al.[51], although it is noticeable that the factors by which the activities are increased are much less than those measured by these workers. The "in situ" technique itself is responsible for a much more active catalyst compared with these previous results[51] and the increase in activity due to the halogenated olefins may be expected to be less as a result. All the initial rates of the catalyst samples after this treatment appear to approach a limit of ~3% min^{-1}, except for the catalyst samples prepared from an unactivated alumina (pretreatment 298K) where the initial rates were very much slower. It would appear that ligands of the molybdenum hexacarbonyl catalyst are replaced by a ligand from the halogenated olefin which facilitates the

breakdown of the catalyst to the active species. In the case of the unactivated alumina samples, the same effect may be taking place but it is anticipated the number of "active sites" is lower as a consequence of the alumina pretreatment and as a result the activity is not enhanced dramatically by the halogenated olefins.

Preliminary infrared experiments[84] suggest that the halogenated olefins trichloroethylene and 3,3,3-trifluoropropene interacted strongly with the molybdenum, displacing carbonyl ligands. This interaction was thought to be in the form of a σ-bond rather than a π-bond, and this appeared to be confirmed by carbon-carbon double bond stretching frequencies.

CHAPTER FIVE

THE ACTIVITY OF SUPPORTED MOLYBDENUM HEXACARBONYL CATALYSTS FOR THE DISPROPORTIONATION OF PROPENE

5.1 Introduction

The work reported on the activity of supported molybdenum hexacarbonyl catalysts[4,38,75] has not included any reference to the variation of the pretreatment temperature of the support which was normally alumina. In this investigation, the molybdenum hexacarbonyl catalysts were supported on several oxide supports, each having undergone evacuation at various temperatures. A detailed study of the variations in catalyst activity from one support to another, with the temperature at which the supports were outgassed before adding the molybdenum hexacarbonyl, and with the temperature of activation, provided information about the nature of the support:molybdenum interaction and about the factors affecting generation of the catalytically active species.

A quantitative comparison of the relative activities of the various catalysts has been made possible by the development of a reproducible method of catalyst preparation by which to compare directly the relative activities of the supported molybdenum hexacarbonyl catalysts for propene disproportionation. The effect of possible poisons on the catalyst surface was also investigated using samples prepared by this method.

5.2 Experimental

Studies of the disproportionation reaction of propene were carried out in the static vacuum system described in Section 3.2. Analysis of the mixture of reacting gases was provided by the G.L.C. unit (Section 3.3) linked to the gas handling system.

Section 3.4 contains the details of the purification and storage of the reactants and information on the supports is contained in Table 3.1. Preparation of the catalyst by the "in situ" technique is described in Section 3.5. The catalyst samples prepared by this technique were all 10% molybdenum hexacarbonyl to support (by weight).

The 10^{-4}kg sample of the catalyst rested on the bottom of the reaction vessel (F_1) of volume $2.54 \times 10^{-4} m^3$. All samples were heated at 373K for 1h before reaction with $3.33 kNm^{-2}$ of propene. For the catalyst activation study, the sample was evacuated at the desired temperature for 1h before reaction with $3.33 kNm^{-2}$ of propene at 298K. Catalyst activities were determined by measuring the initial rate of disproportionation to ethylene and butenes at this temperature. For low activities (initial rate less than 1% min^{-1}) the initial rates were determined directly from plots of propene concentration against time extrapolated to zero time. Where the activity was high, the initial rate was calculated from the second order rate constant as described in Section 4.3. The uncertainty in the initial rates and hence the activities determined by either of these methods was less than $\pm$10%. For the most active catalysts the rate of disproportionation was likely to be diffusion limited, which would impose an upper limit on the measured

activities. The activities are also expressed as initial rates of propene disproportionation at 3.33kNm^{-2} and 298K per unit surface area of support, for comparison.

Spent catalyst samples were analysed for molybdenum by X-ray fluorescence (alumina supported catalysts) or atomic absorption spectrophotometry (silica-alumina supported catalysts). Spent catalyst samples were also examined by X-ray diffraction, but no evidence was found for the existence of any new phase.

5.3 Results

Molybdenum hexacarbonyl proved to be an active catalyst for propene disproportionation when supported on several oxides. The activity was dependent on the type of support and the temperature of pretreatment of each support. Similarly, activity of the catalyst was studied by varying the activation temperatures of the catalyst system.

The stoichiometry of the equation believed to represent the disproportionation of propene:

$$2\ C_3H_6 \rightleftharpoons C_2H_4 + C_4H_8$$

suggested that equal quantities of ethylene and butene should be formed. As will be shown, this was never exactly accomplished due to the preferential adsorption of butene, although in certain cases it was closely approached. A typical product distribution for the disproportionation of 3.33kNm^{-2} of propene at 298K on a 10% molybdenum hexacarbonyl catalyst supported on γ-alumina is shown in Figure 5.1. Although but-1-ene is formed by double bond isomerization of the but-2-ene, it is present only to the extent of 1% and hence is not shown in Figure 5.1.

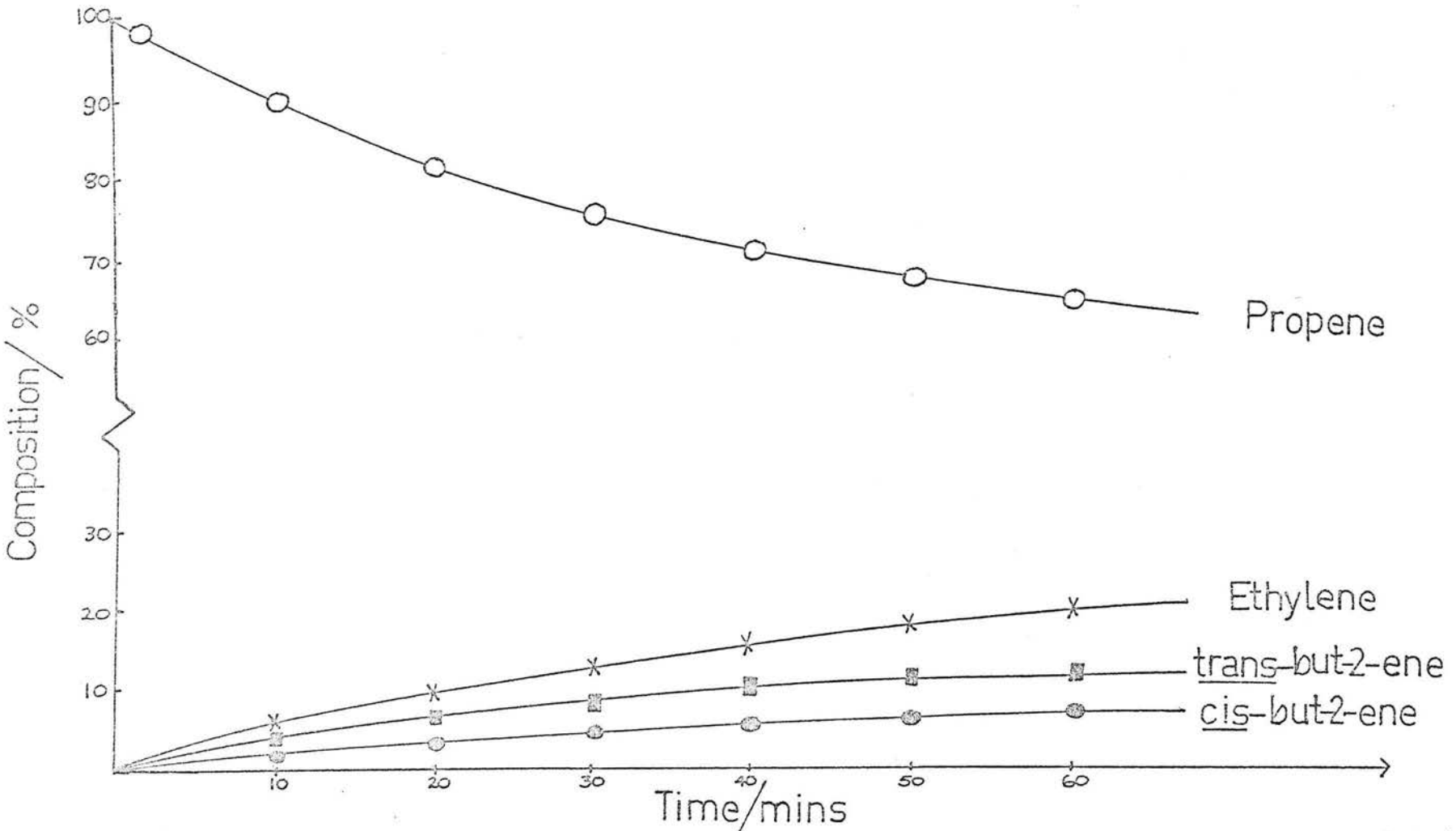


Fig.5.1. Propene Disproportionation Reaction at 298 K. Propene Pressure 3·33 kNm^{-2}

5.3.1 Support Pretreatment

The activities of silica, alumina, silica-alumina and magnesium oxide supported catalysts were determined as a function of the temperature at which the support was outgassed *in vacuo* before adding the molybdenum hexacarbonyl. The results are contained in Tables 5.1 to 5.4 and are represented graphically in Figures 5.2 to 5.5. In all cases the supported catalysts were activated *in vacuo* for 1h at 373K after pretreatment. Any excess molybdenum hexacarbonyl was removed from the support during activation. In order to determine whether the catalyst activity was directly related to the amount of molybdenum retained by the support, the percentage of molybdenum in spent catalyst samples was measured as a function of the support pretreatment temperature for a series of γ-alumina and silica-alumina supported catalysts; the results are given in Table 5.5 and shown graphically in Figure 5.6. Blank experiments were carried out with the supports alone after outgassing at 973K but these showed no activity for propene disproportionation at 298K.

The activities of zeolite supported catalysts as a function of outgassing temperature of support before addition of the molybdenum hexacarbonyl are contained in Tables 5.6 and 5.7. Catalysts supported on charcoal which had been outgassed at 573K for 1h were not active for propene disproportionation at 298K.

TABLE 5.1

10% $Mo(CO)_6$ supported on silica

Pretreatment Temperature/K	Initial Rate/(% min^{-1})
298	3.98, 3.95
373	1.40
573	0.81
673	0.82
923	1.40, 1.70
1023	0.62, 1.00

TABLE 5.2

10% $Mo(CO)_6$ supported on alumina

Pretreatment Temperature/K	Initial Rate/(% min^{-1})
298	5×10^{-3}, 6×10^{-3}
373	0.03
423	0.10
473	0.29
573	0.78, 1.00
673	0.82, 0.71
773	0.63, 0.61
873	0.07
923	0.09
998	0.17
1058	0.10, 0.12

TABLE 5.3

10% $Mo(CO)_6$ supported on silica-alumina

Pretreatment Temperature/K	Initial Rate/(% min^{-1})
298	0.16, 0.09
373	0.27
523	0.46
673	0.64
923	0.80, 0.72
1023	0.44

TABLE 5.4

10% $Mo(CO)_6$ supported on magnesium oxide

Pretreatment Temperature/K	Initial Rate/(% min^{-1})
298	2×10^{-3}, 1.2×10^{-3}
473	4×10^{-3}
573	8×10^{-3}
673	0.013
923	0.040
1023	0.032, 0.035
1073	0.016

TABLE 5.5

Molybdenum analyses for supported $Mo(CO)_6$ catalysts

Pretreatment Temperature/K	298	423	573	923	1023	1073
Alumina Supported Sample	0.4	0.45	0.60	0.90		1.0
Silica-alumina Supported Sample	0.23			0.76	0.93	

TABLE 5.6

10% $Mo(CO)_6$ supported on Na 13X zeolite

Pretreatment Temperature/K	Initial Rate/(% min^{-1})
298	6×10^{-3}
673	0.12
923	0.02
1023	0.11
673*	0.20

* Catalyst activated at 673K also for 1h.

TABLE 5.7

10% $Mo(CO)_6$ supported on $NH_4^{III}X$ zeolite

Pretreatment Temperature/K	Initial Rate/(% min^{-1})
673	0.04, 0.05
673*	0.40, 0.60

* Catalyst activated at 673K also for 1h.

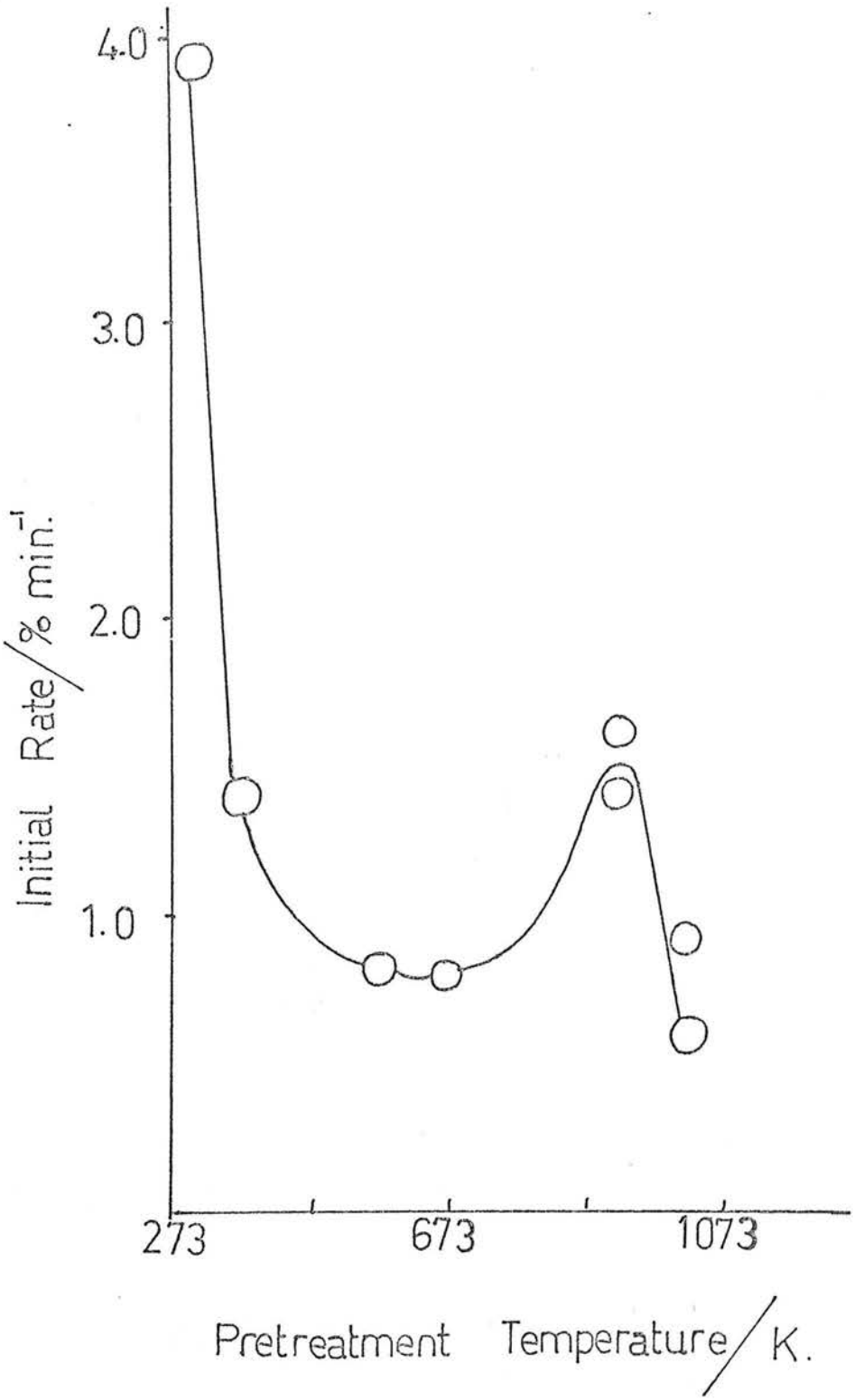


Fig. 5.2. Variation in activity of catalyst with pretreatment of the silica support.

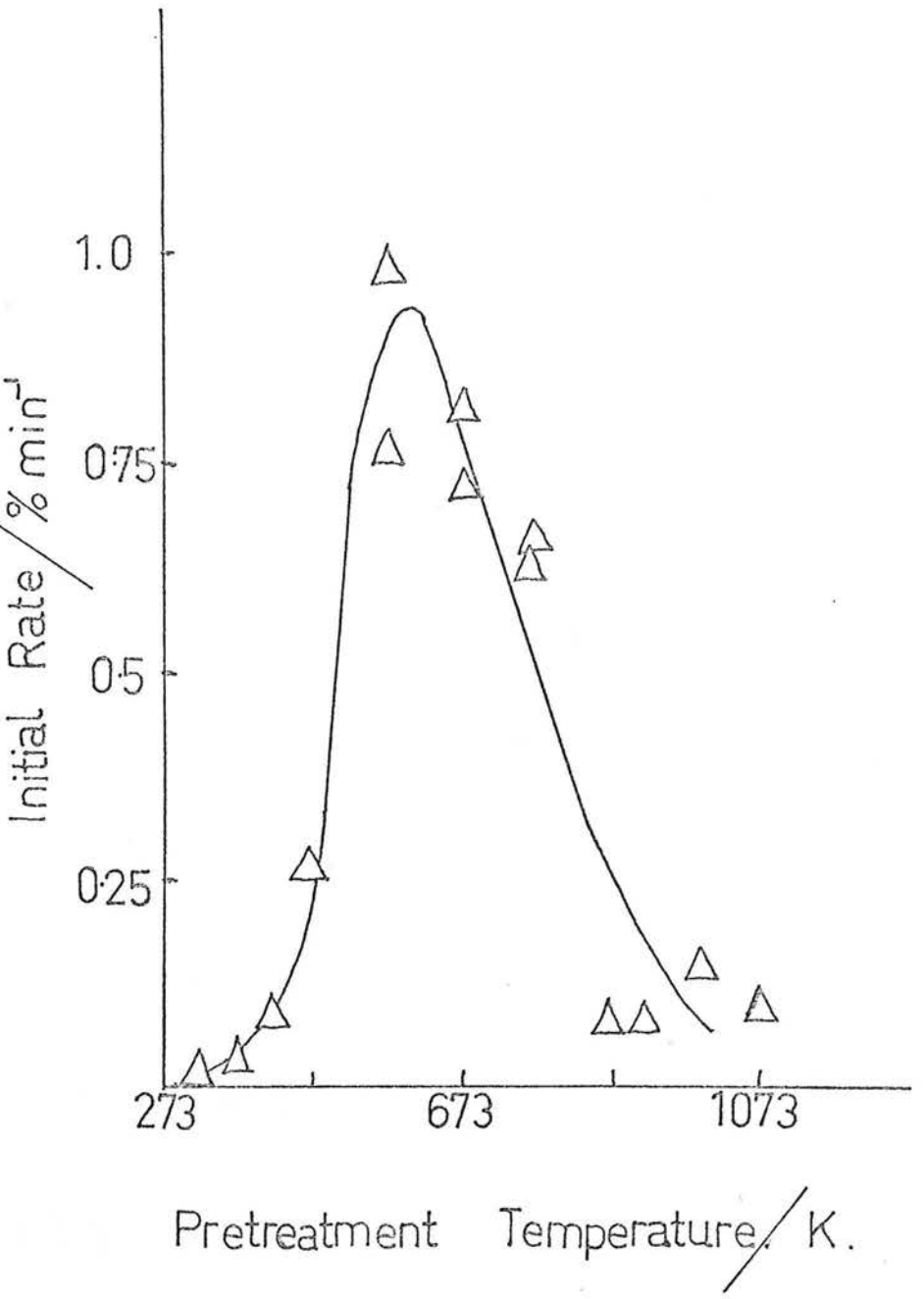


Fig. 5.3. Variation in activity of catalyst with pretreatment of the alumina support.

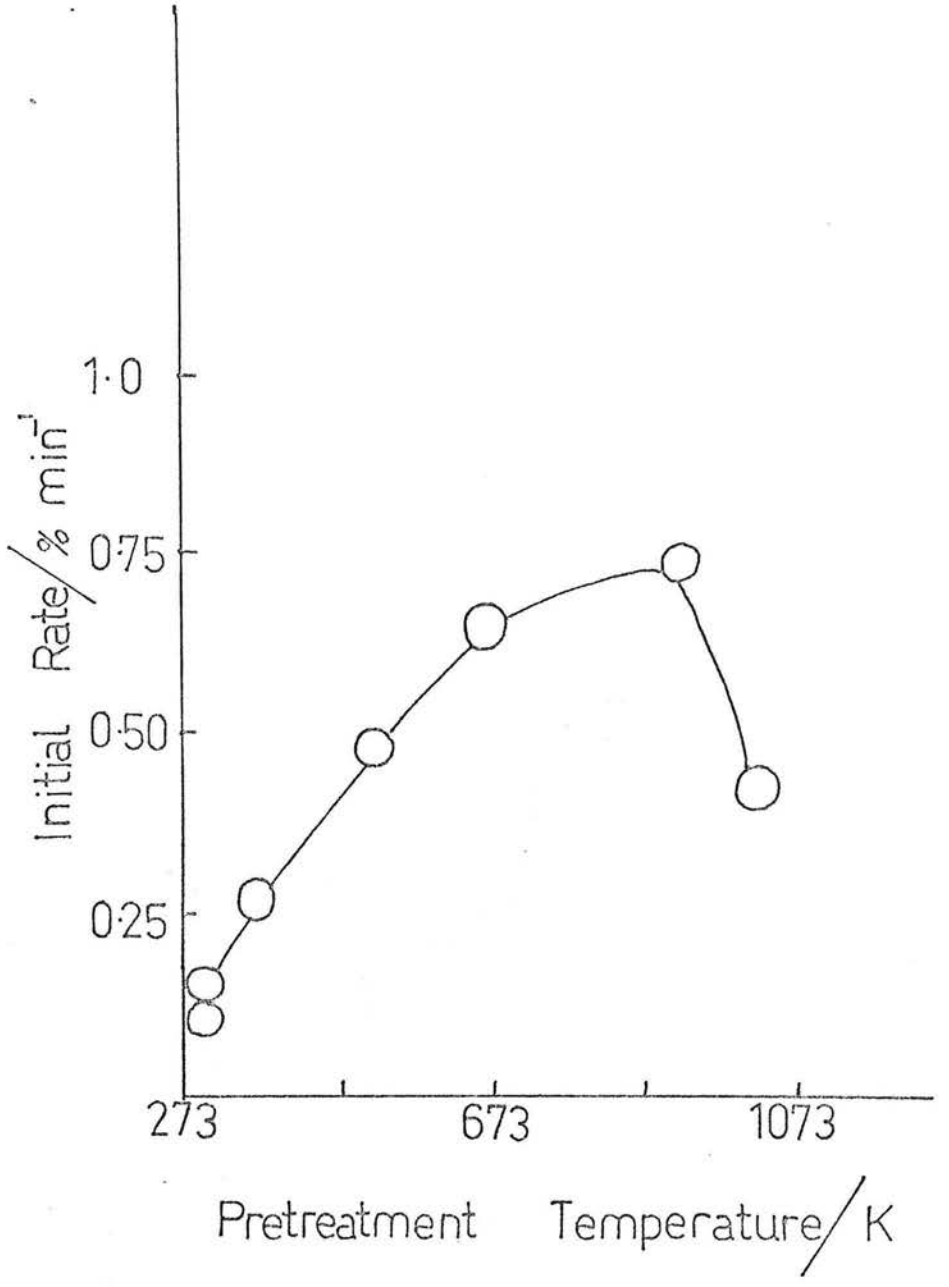


Fig. 5.4. Variation in activity of catalyst with pretreatment of the silica-alumina support.

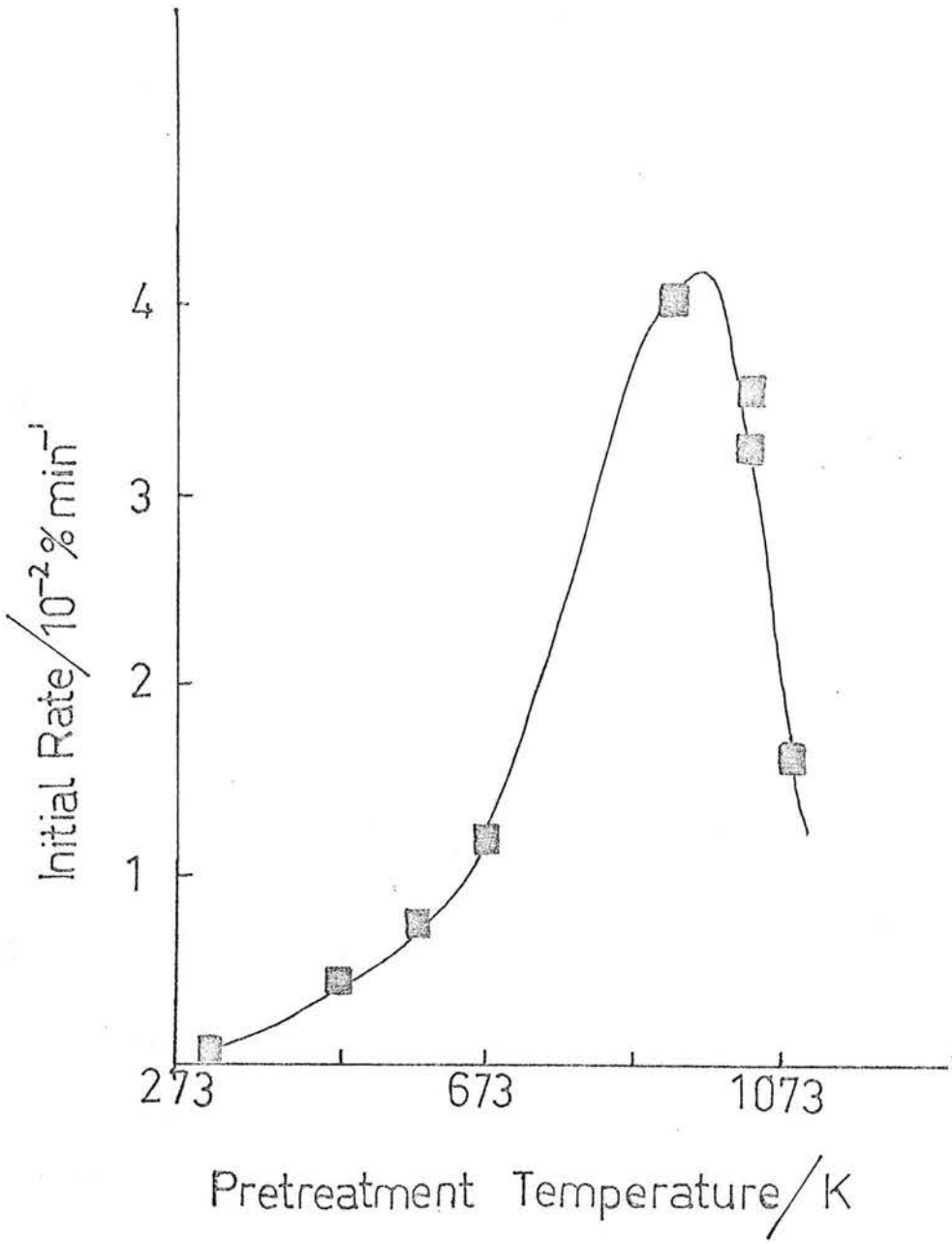


Fig. 5.5. Variation in activity of catalyst with pretreatment of the magnesium oxide support.

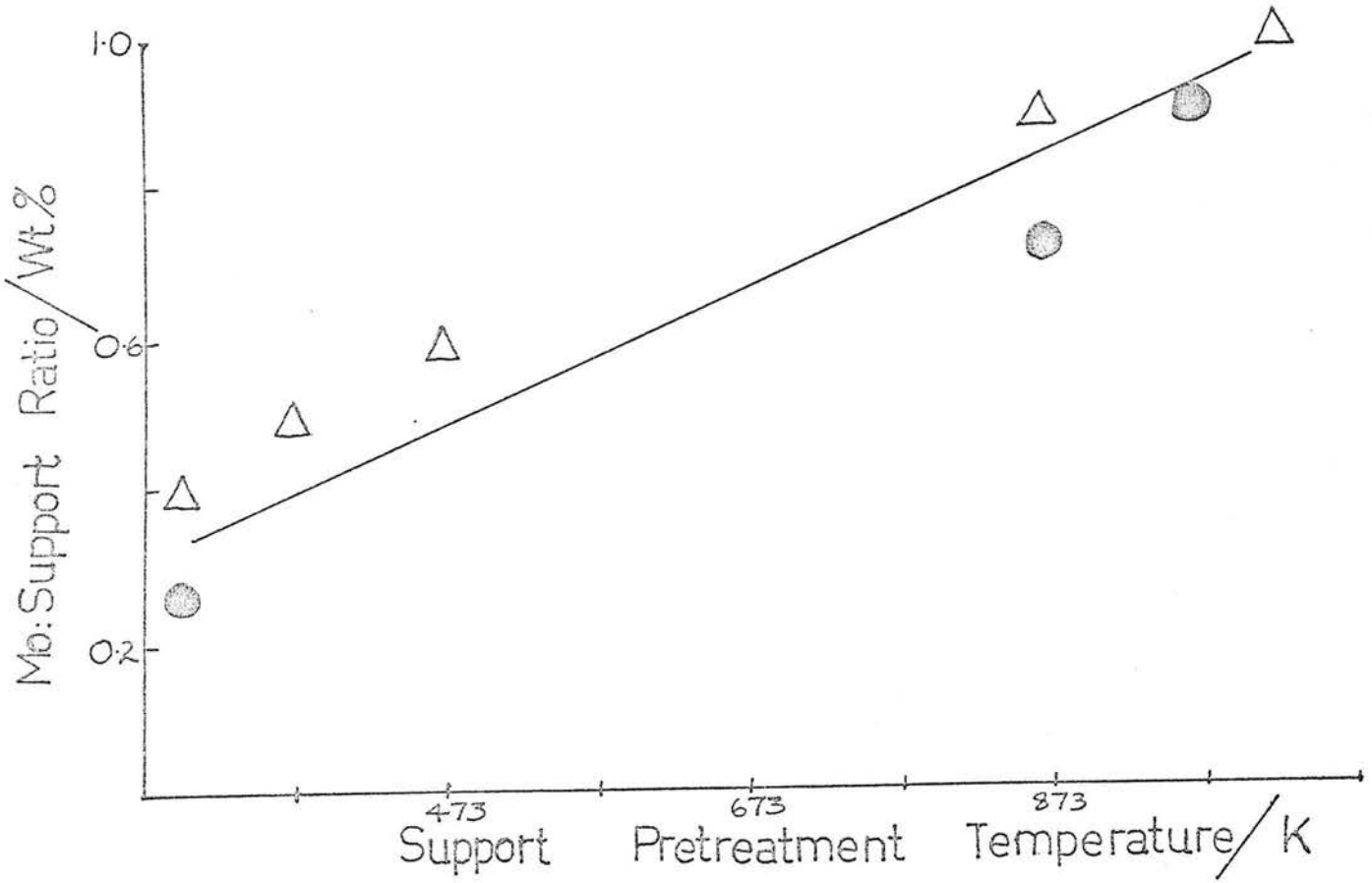


Fig. 5.6. % Mo as a function of Support Pretreatment.
△, γ-alumina; ●, silica–alumina.

5.3.2 Catalyst Activation

The variations in activity with the temperature at which the catalysts were activated after addition of molybdenum hexacarbonyl to the support were also investigated for silica, γ-alumina, silica-alumina and magnesium oxide. For each support two series of experiments were performed - one with the support pretreated at 298K, and one with the support pretreated at the temperature found to give maximum activity (i.e. 573K for alumina, 923K for silica-alumina, and 1023K for magnesium oxide). In the case of the silica supported catalysts maximum activity was obtained on a support pretreated at 298K, so a second series of experiments was carried out with a silica support pretreated at 1023K. Catalysts were activated *in vacuo* initially at 373K for 1h and then for 1h at each successive temperature, activity being measured after each activation step. The results are presented in Tables 5.8 to 5.11 and represented graphically in Figures 5.7 to 5.10.

In the case of the silica supported catalysts, two samples were prepared to check the accuracy of the activities measured at the various temperatures. In both samples, the silica was pretreated at 298K, and after impregnation, the samples were activated at 473K and 673K. The initial rates of disproportionation of 3.33kNm^{-2} at 298K were 5.60% min^{-1} and 0.74% min^{-1} respectively. These activities coincided with those contained in Table 5.8.

The conditions necessary for obtaining the maximum activity for propene disproportionation from the four catalysts studied are summarised in Table 5.12.

TABLE 5.8

10% $Mo(CO)_6$ supported on silica

Activation Temperature/K	Initial Rate/(% min^{-1})	
	SiO_2 (298K)	SiO_2 (1023K)
373	3.95	1.03
473	5.80	2.50
573	1.25	0.45
673	0.80	0.30
803		1.52
823	1.78	
923	1.28	1.60
1023		1.02
1048	0.82	

TABLE 5.9

10% $Mo(CO)_6$ supported on alumina

Activation Temperature/K	Initial Rate/(% min^{-1})	
	Al_2O_3 (573K)	Al_2O_3 (298K)
373	0.44	6×10^{-3}
473	1.10	0.09
573	0.32	6×10^{-3}
673	0.05	0.03
803	7×10^{-3}	0.04
923	0.07	0.07
1023		0.08
1073	0.09	

TABLE 5.10

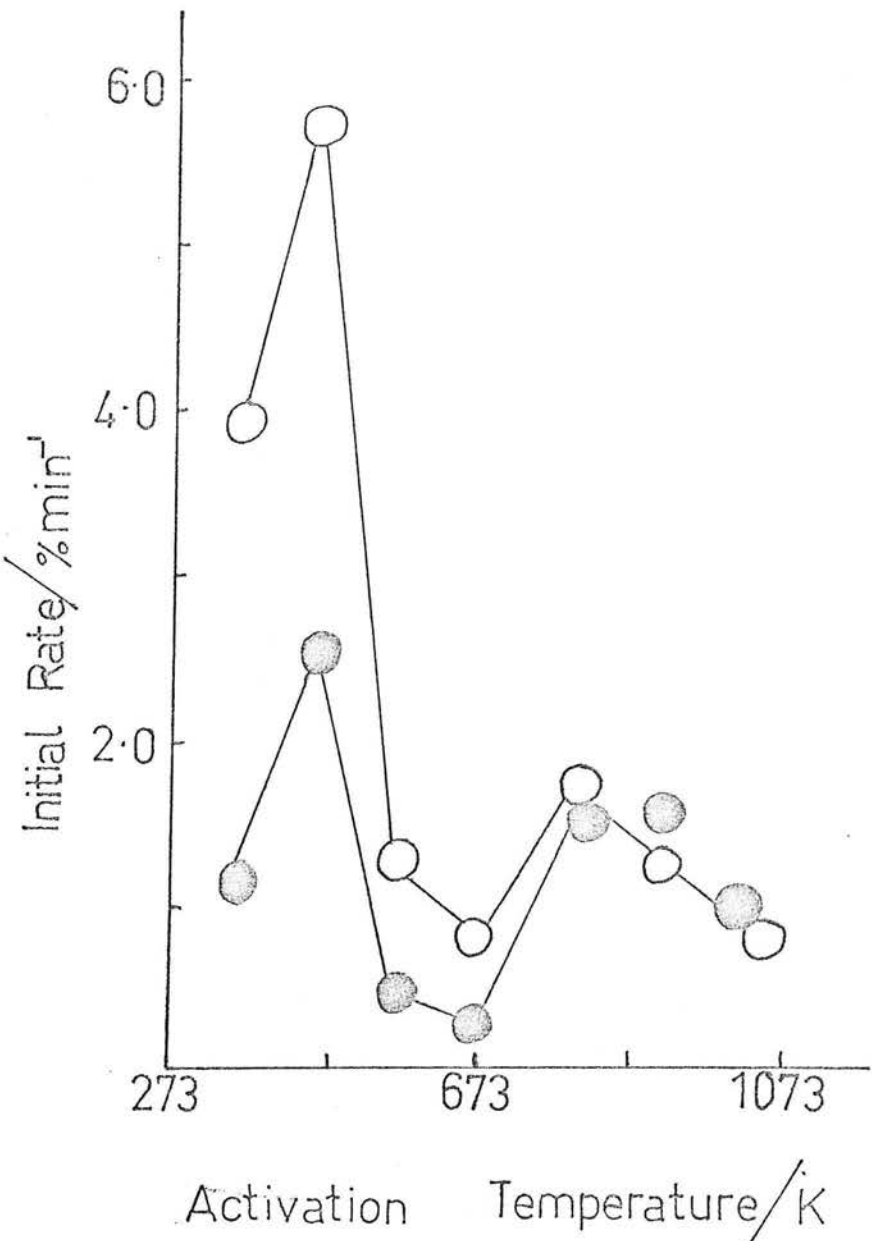
10% $Mo(CO)_6$ supported on silica-alumina

Activation Temperature/K	Initial Rate/(% min^{-1})	
	SiO_2 Al_2O_3 (923K)	SiO_2 Al_2O_3 (298K)
373	0.72	0.09
473	2.64	0.42
573	2.42	0.27
673	2.14	0.45
803	2.89	0.72
923	2.25	1.03
1073	2.00	0.85

TABLE 5.11

10% $Mo(CO)_6$ supported on magnesium oxide

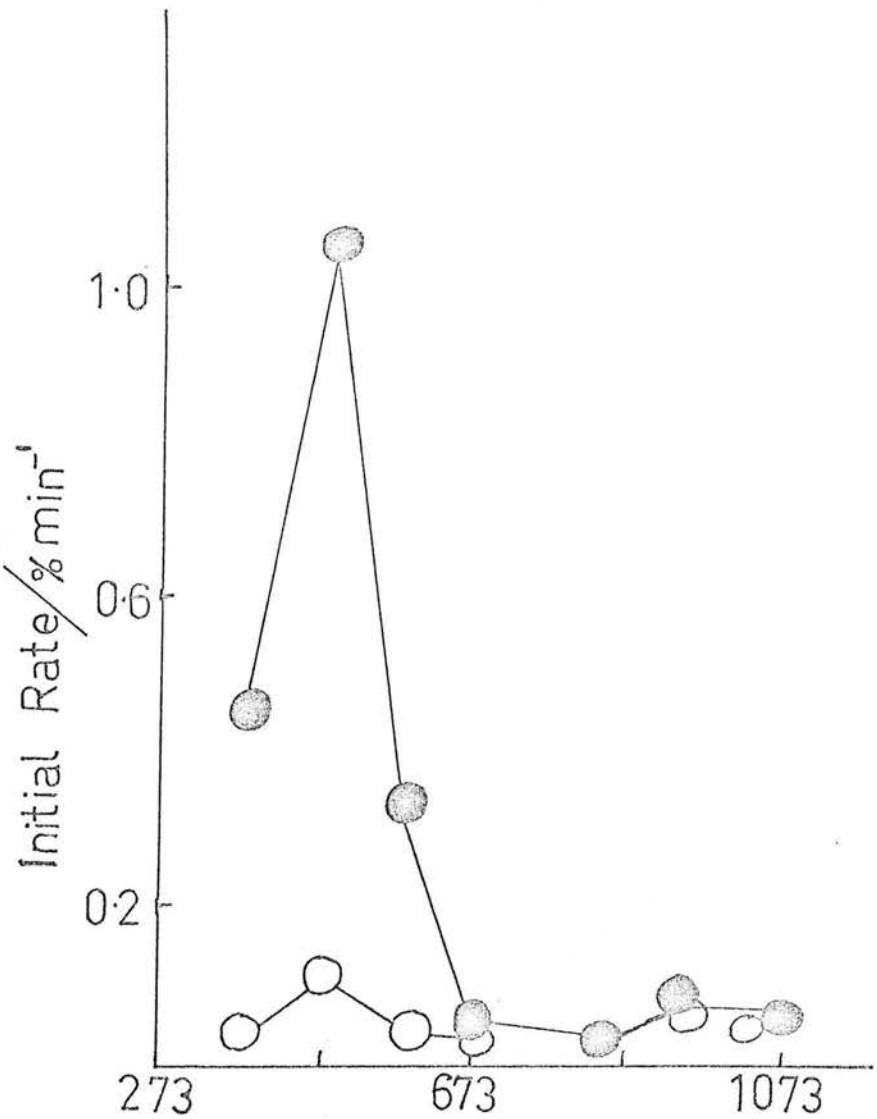
Activation Temperature/K	Initial Rate/(% min^{-1})	
	MgO (1023K)	MgO (298K)
373	.04	2×10^{-3}
473	.26	1×10^{-3}
573	1.40	2×10^{-3}
673	0.04	.02
823	0.03	2×10^{-3}



○, silica pretreated at 298K.

●, " " " 1023K.

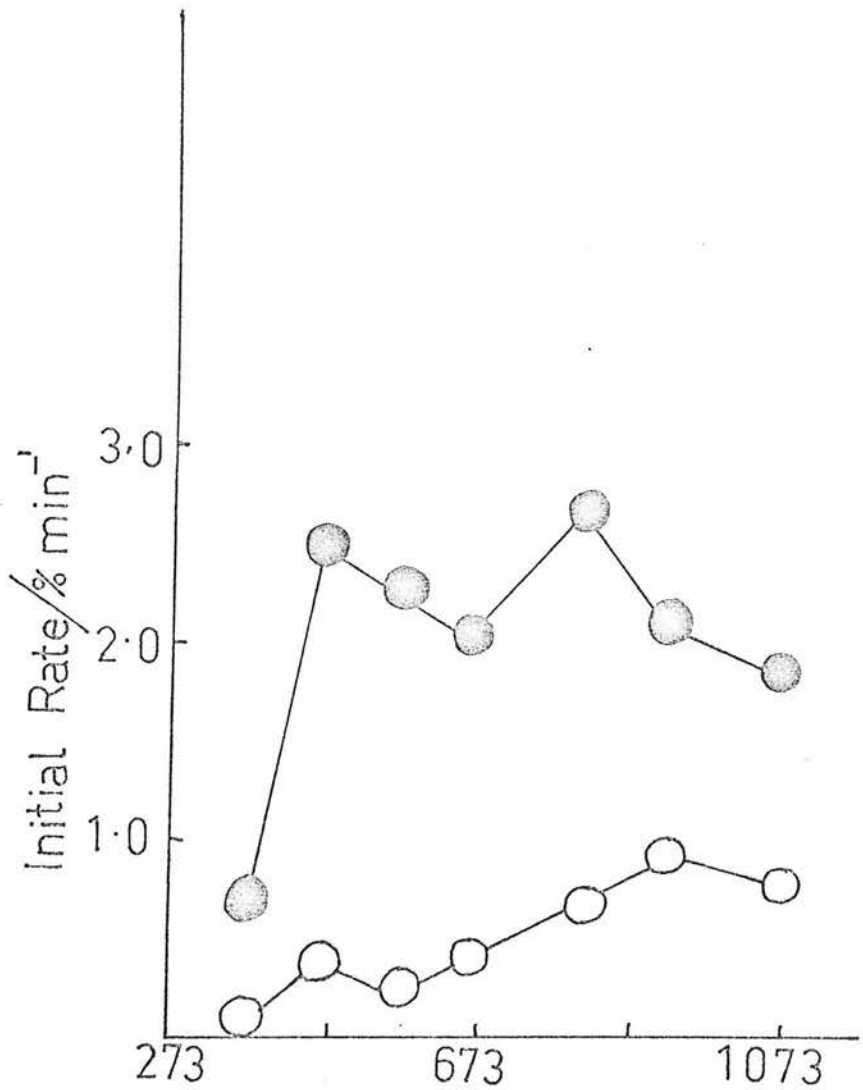
Fig. 5.7. Variation in the activity of the silica supported catalyst with activation temperature.



O, alumina pretreated at 298 K.

●, " " " 573 K.

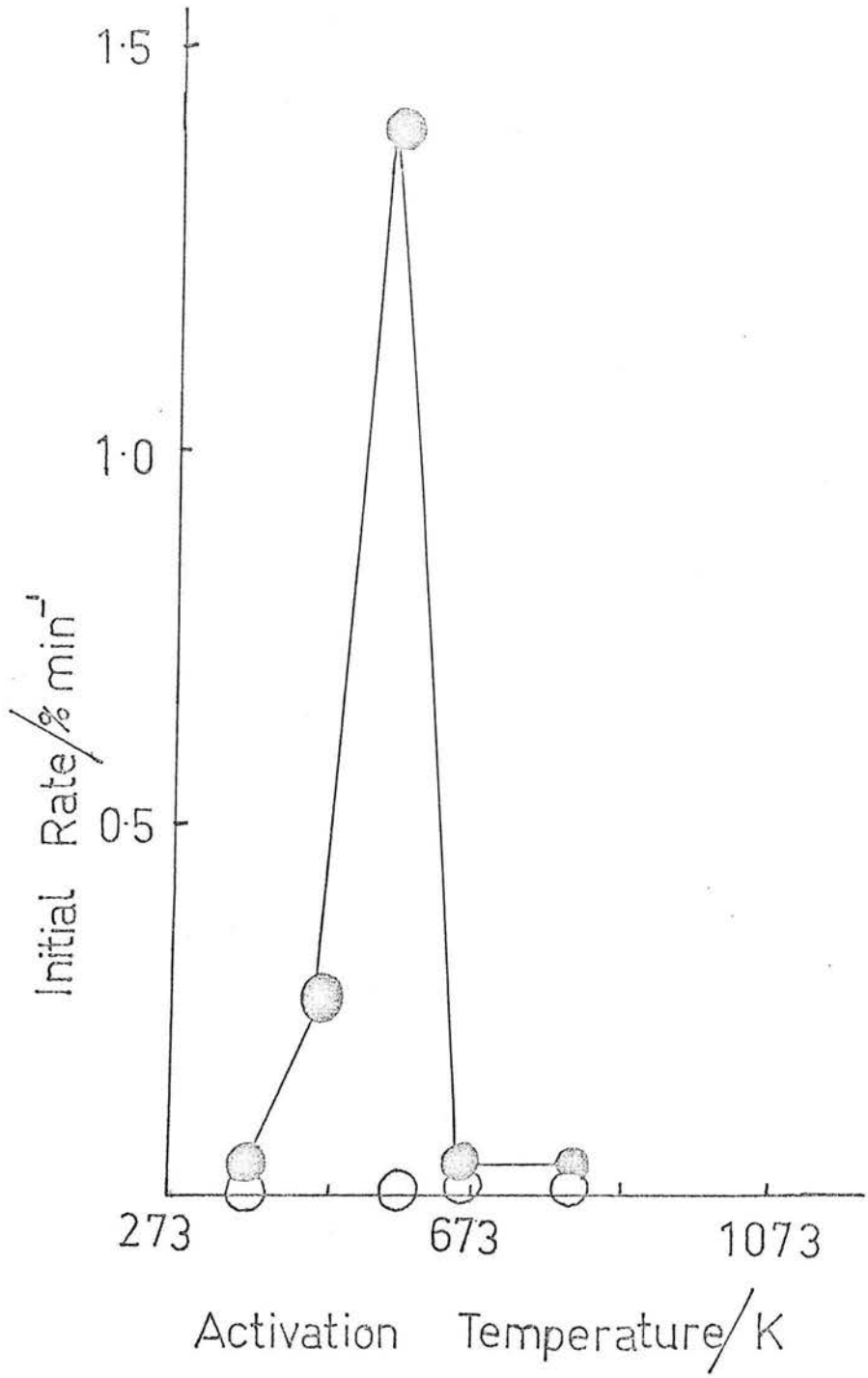
Fig. 5.8 Variation in the activity of the alumina supported catalyst with activation temperature.



O, silica-alumina pretreated at 298 K.

●, " " " 1023 K.

Fig. 5.9. Variation in the activity of the silica alumina supported catalyst with activation temperature.



O, magnesium oxide pretreated at 298 K.

●, " " " " 1023 K.

Fig. 5.10. Variation in the activity of the magnesium oxide supported catalyst with activation temperature.

TABLE 5.12

Maximum Rates of Propene Disproportionation

Support	Support Pretreatment Temperature/K	Catalyst Activation Temperature/K	Initial Rate*/ (% $min^{-1}m^{-2}$)
γ-Al_2O_3	573	473	0.06
SiO_2	298	473	0.12
SiO_2-Al_2O_3	923	823	0.14
MgO	1023	573	0.29

* Propene pressure = 3.33kNm^{-2}, T = 298K

Effect of Support Surface Area on Product Distribution

Table 5.13 includes the percentage product distributions for the various supported catalysts. Each catalyst was tested for optimum activity, i.e. maximum support pretreatment and maximum catalyst activation. The surface areas of the supports are included in the table. Each percentage distribution represents the amount of reaction at t = 30 mins in each case.

TABLE 5.13

Catalyst	$C_2^=$	$C_3^=$	2-$C_4^=$(trans)	2-$C_4^=$(cis)
$Mo(CO)_6/MgO$	9.5	81.2	7.0	2.4
(s.a. $\cdot 49 m^2 kg^{-1}$)			*Ratio = 0.99	
$Mo(CO)_6/Al_2O_3$	11.0	79.6	7.1	2.4
(s.a. $1.81 m^2 kg^{-1}$)			Ratio = 0.86	
$Mo(CO)_6/SiO_2$	19.2	65.4	11.7	3.7
(s.a. $4.71 m^2 kg^{-1}$)			Ratio = 0.80	
$Mo(CO)_6/SiO_2Al_2O_3$	17.6	66.8	11.8	3.8
(s.a. $2.08 m^2 kg^{-1}$)			Ratio = 0.89	
$Mo(CO)_6/NH_4^{III}X$ zeolite	12.3	86.5	0.8	0.4
(s.a. $\sim 9.00 m^2 kg^{-1}$)			Ratio = 0.10	

* Ratio $\frac{C_4^=}{C_2^=}$

[all surface areas $\times 10^5$]

5.3.3 Poisoning Experiments

Acetylene Treatment

Acetylene was used as a possible poison for a 10% molybdenum hexacarbonyl catalyst supported on alumina. The support had been pretreated at 573K for 1h. The results are shown in Table 5.14 for the disproportionation of 3.33kNm^{-2} propene at 298K.

TABLE 5.14

Catalyst	Initial Rate/ (% min^{-1})
$Mo(CO)_6/\gamma\text{-}Al_2O_3$	1.20
" + 0.11kNm^{-2} acetylene	0.28
" + 0.04kNm^{-2} acetylene	0.85
" + 0.40kNm^{-2} acetylene	0.47

The catalyst sample was outgassed at 313K for 40 mins before admission of the dose of acetylene to the reaction vessel. A pressure of 0.11kNm^{-2} of acetylene was calculated as sufficient to cover all the molybdenum sites on the catalyst surface.

Oxygen Treatment

A (10^{-4}kg) sample of 10% molybdenum hexacarbonyl on alumina of known activity was allowed to come in contact with 0.53kNm^{-2} of oxygen for 5 mins, and after evacuation for 30 mins, the activity of the sample was measured at 298K. This procedure was repeated several times and the initial rates of propene disproportionation for the sample after treatment with oxygen are presented in Table 5.15 and shown graphically in Figure 5.11.

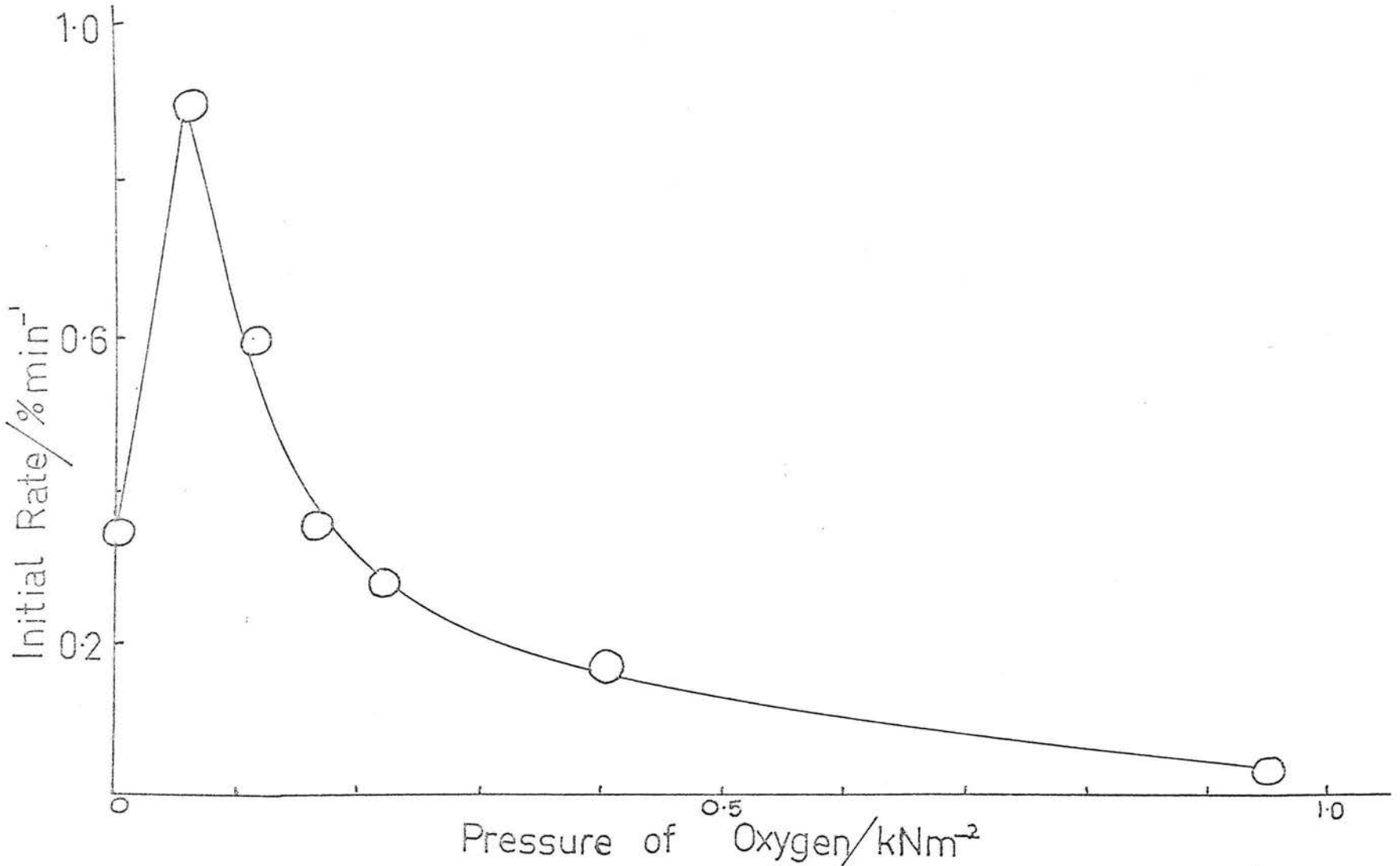


Fig. 5.11. Effect of oxygen on the activity of the $Mo(CO)_6/Al_2O_3$ catalyst.

In all cases the dose of propene was $3.33 kNm^{-2}$.

TABLE 5.15

Catalyst	Initial Rate/ ($\% min^{-1}$)
10% $Mo(CO)_6/\gamma\text{-}Al_2O_3$	0.34
" + $0.53 kNm^{-2}$ O_2	0.81
" + $0.53 kNm^{-2}$ O_2	0.59
" + $0.53 kNm^{-2}$ O_2	0.35
" + $0.53 kNm^{-2}$ O_2	0.28
" + $2.00 kNm^{-2}$ O_2	0.17
" + $5.32 kNm^{-2}$ O_2	0.04

Hydrogen Treatment of the γ-Alumina Support

A 10% molybdenum hexacarbonyl on alumina was prepared using a 10^{-4}kg sample of alumina which had been treated with a dose of hydrogen. After outgassing the alumina sample at 573K for 1 hour, $26.60 kNm^{-2}$ of hydrogen was admitted to the sample and the reaction vessel heated at 573K for 3h. The catalyst sample was then prepared in the normal manner and the sample exposed to $3.33 kNm^{-2}$ of propene and its activity measured. An initial rate of 0.80% min^{-1} was recorded at 298K.

5.4 Discussion

The following points emerge from the results obtained from "Support Pretreatment" and "Catalyst Activation" presented in Tables 5.1 to 5.12.

(a) the activity of supported molybdenum hexacarbonyl catalysts depends on the support used.

(b) for any one particular support, the activity depends on the way in which the support surface is pretreated before addition of the molybdenum hexacarbonyl.

(c) the variations in activity with support treatment are not due to variations in the amount of molybdenum retained by the support.

(d) the activity depends on the temperature of activation after addition of molybdenum hexacarbonyl to the support.

Points (a), (b) and (c) indicate clearly the importance of a molybdenum:support interaction in the formation of the active catalyst. Molybdenum hexacarbonyl is sufficiently volatile to ensure that any excess not interacting with the support will be rapidly removed on evacuation at room temperature. Infrared studies[80] of molybdenum hexacarbonyl on fully hydrated supports showed that the initial interaction between the hexacarbonyl and the support can be envisaged as involving replacement of one carbonyl ligand in the co-ordination sphere of the molybdenum by a surface hydroxyl group to form a pentacarbonyl species which then decomposes further to leave eventually a molybdenum species containing no carbonyl ligands. For silica supported catalysts, maximum activity is obtained on a support outgassed at room temperature before addition of the molybdenum hexacarbonyl.

Such pretreatment should remove most of the adsorbed water from the surface, but is insufficient to cause loss of surface hydroxyl groups[85]. Thus the maximum activity may be associated with the presence of a maximum concentration of hydroxyl groups on the support. If the initial interaction between molybdenum hexacarbonyl and the silica support is occurring in the manner suggested, maximum dispersion of the molybdenum hexacarbonyl will be achieved on the fully hydroxylated support. Likewise, the maximum in the activity of alumina supported catalysts at a support pretreatment temperature of 573K may be attributed to the presence of a maximum concentration of surface hydroxyl groups on the support after removal of adsorbed water, since alumina surfaces are dehydroxylated less readily than silica, and complete removal of adsorbed water is more difficult[86].

The fall-off in activity of alumina supported catalysts on supports pretreated above 673K may be correlated with the onset of extensive dehydroxylation of the support, but is not due to a reduction in the total amount of molybdenum retained by the support. Interaction of molybdenum hexacarbonyl with the sites available on a dehydroxylated alumina support evidently does not favour formation of the catalytically active species. The spectroscopic studies have so far been confined to hydrated supports, so that the nature of any interaction between molybdenum hexacarbonyl and, for example, Lewis acid sites on a dehydroxylated alumina support remains unknown. It is likely, however, that molybdenum hexacarbonyl is less well dispersed on dehydroxylated supports, although the X-ray diffraction measurements have not revealed the existence of any bulk molybdenum-containing phase on such supports. Molybdenum analyses were

not obtained for silica supported catalysts, but the fall-off in activity on dehydroxylated silica supports parallels that observed on alumina, and is presumably due to the same causes. It may be noted that the activity does not fall completely to zero on extensively dehydroxylated supports. The apparent secondary maximum in Figure 5.2 lies outside the range of experimental uncertainty, and its origin is not clear.

The behaviour of silica-alumina supported catalysts is intermediate between that of silica and alumina supported catalysts in that, although there is a significant activity on a support pretreated at room temperature, complete removal of adsorbed water by pretreatment at higher temperature[87] leads to enhanced activity, and the activity falls on an extensively dehydroxylated support. This behaviour is not unexpected, since the silica-alumina with an alumina content of 45% is likely to contain conglomerates of the pure alumina phase. The broad maximum in the activity of silica-alumina supported catalysts for support pretreatment temperatures between 673K and 873K may thus be attributed to the presence of a maximum concentration of free hydroxyl groups on the support, leading to maximum dispersion of the molybdenum hexacarbonyl, although this description is probably oversimplified in that the silica-alumina surface contains at least two different types of hydroxyl groups, which may differ in behaviour.

In contrast, the activity of magnesium oxide supported catalysts is extremely low unless the support is pretreated above 673K. We believe that this anomalous behaviour is due to the greater basicity of hydroxyl groups on magnesium oxide.

The infrared studies[80] have shown that the hydroxyl groups on magnesium oxide retard the decomposition of molybdenum hexacarbonyl by stabilising intermediate subcarbonyl species to a greater extent than on alumina or silica, and it seems that the catalytically active species can be formed readily only on the dehydroxylated support, but the nature of the interaction between molybdenum hexacarbonyl and dehydroxylated magnesium is not known.

The catalysts supported on zeolites experienced adsorption of the butenes on the catalyst surface due to the very high surface area of these supports. The ammonium-exchanged zeolite appeared to be the most active and a fairly rapid initial rate of disproportionation was observed when, after pretreatment at 673K, the support was impregnated in the normal way and the catalyst activated at 673K. This procedure was carried out in accordance with the preparation of molybdenum-loaded zeolites[88]. Although, in the case of Na 13X zeolite, a pretreatment study was attempted, no real trend was observed. It certainly appeared necessary to evacuate the zeolite support to at least 673K in order to remove the adsorbed water, although above 823K it is feasible that the cage structure of the zeolites breaks down considerably[89]. The effect of butene adsorption compared with the rest of the supports tested was quite marked, and the measurement of accurate initial rates was somewhat upset as a result.

Activation of supported molybdenum hexacarbonyl catalysts has been shown to cause oxidation of the molybdenum[90]. Alumina and silica-alumina surfaces have sites capable of oxidising aromatic hydrocarbons[91], but such sites are generated only on

outgassing at high temperatures, and have not been observed on silica or magnesium oxide surfaces, so that they are unlikely to be involved in the formation of active catalysts. The possibility of oxidation being caused by traces of residual molecular oxygen[92] appears unlikely in view of the reproducibility of catalyst activities and the wide variations in the behaviour of different supports, although it cannot be completely ruled out, particularly for supports pretreated at low temperatures. It would seem, rather, that the oxidation must be associated in some way with the hydroxyl groups on silica, alumina and silica-alumina, since it occurs on the fully hydroxylated supports under very mild conditions. Charge transfer to surface hydroxyl groups has been suggested to account for the "hydrogen-bonding" of certain aromatic hydrocarbons on silica surfaces[93], and we might envisage a similar charge transfer from molybdenum to form the catalytically active species. While there is no direct experimental evidence to support such a suggestion, it is consistent with the low activity of catalysts supported on hydrated magnesium oxide, since charge transfer to the basic hydroxyl groups on magnesium oxide will not occur as readily as on silica or alumina.

The variations in activity with the temperature at which catalysts are activated after addition of molybdenum hexacarbonyl to the support (Figures 5.7 to 5.10) can be accounted for in terms of oxidation of the molybdenum on the support during activation. One feature common to all catalysts is the occurrence of a maximum in the activity for an activation temperature of 473K (on silica, alumina, and silica-alumina supports) or 573K

(on magnesium oxide). This maximum activity is attributed to the formation of a maximum concentration of the catalytically active molybdenum species by oxidation from molybdenum (O), assuming that at higher activation temperatures the active species is further oxidised. It was suggested from the e.s.r. studies that the active species may be molybdenum (IV), which on activation above 473K is further oxidised to molybdenum (V) (in tetrahedral co-ordination)[90]. Variation of the support pretreatment is seen from Figure 5.6 to affect the fraction of the total molybdenum able to form the active species, but not the rate of formation.

There is some suggestion in Figures 5.7 to 5.10 of a secondary maximum in the activity at high activation temperatures. This effect is particularly pronounced for silica and silica-alumina supported catalysts. High temperature activation in vacuo of supported molybdenum trioxide catalysts causes loss of oxygen and reduction from molybdenum (VI) to lower oxidation states[94,95]. In view of the demonstrated similarity[90] between supported molybdenum trioxide catalysts and supported molybdenum hexacarbonyl catalysts after high temperature activation, these secondary maxima may be attributed to formation of the active molybdenum species by reduction from higher oxidation states. Since reduction of supported molybdenum (VI) below oxidation state (IV) does not readily occur at temperatures below 873K[96], this provides some support for the suggestion that the active species may be molybdenum (IV). The ease with which back-reduction can occur appears to vary from one support to another. It is not clear why the secondary maximum is so

much more pronounced on silica-alumina supports; possibly the active species is more stable with respect to further oxidation on silica-alumina than on the other supports.

It appears that the role of the support in supported molybdenum hexacarbonyl catalysts is two-fold; initially to disperse the molybdenum hexacarbonyl, and then to assist oxidation of the molybdenum to form the active species. Maximum activity on any particular support is achieved when both of these conditions are optimised. We can account for the results presented here in terms of the model of the active catalyst deduced from spectroscopic studies, but definite identification of the active species is still not possible.

The interesting results obtained from the reaction of ethylene and propene on an $Mo(CO)_6/Al_2O_3$ catalyst[97] indicated that ethylene was more strongly adsorbed than butenes, and as a result the $\frac{C_2^=}{C_4^=}$ ratio obtained in the disproportionation reaction of propene was quite small (<1). These workers explained the formation of propene from ethylene from this conclusion. The extensive work on supported molybdenum hexacarbonyl catalysts outlined in this chapter did not record $\frac{C_2^=}{C_4^=}$ ratios of this order. The results obtained from the various supported $Mo(CO)_6$ catalysts showed $\frac{C_2^=}{C_4^=}$ ratios to be greater than unity - the preferential adsorption of the butenes being conclusive.

The results obtained from the poisoning experiments indicate that acetylene is not an ideal poison for the alumina supported molybdenum hexacarbonyl catalyst. Addition of $0.11 kNm^{-2}$ acetylene appeared to poison the catalyst to a certain degree but subsequent admissions of acetylene to the catalyst failed to reduce the activity in any marked manner.

The effect of oxygen on the activity of the alumina supported catalyst was more pronounced (Figure 5.11), and it appeared that oxygen, after initially enhancing the activity, eventually decreased the activity on addition of larger doses. This may be explained by comparing the results obtained from e.s.r. measurements of supported molybdenum hexacarbonyl catalysts[80]. In the case of an alumina supported catalyst activated at 373K it was found that the active species was not in its most abundant until activation at 473K, whereupon maximum activity for that catalyst was observed. This was explained by oxidation of the molybdenum in lower oxidation state (0) to that of the supposed active species in a higher oxidation state. Similarly, the initial dose of oxygen is thought to have this effect of oxidation of the molybdenum to this oxidation state of the active species. Addition of more oxygen may lead to further oxidation of the molybdenum to an even higher oxidation state of Mo which is not responsible for the activity for the disproportionation of propene.

The admission of hydrogen to the activated alumina support did not appear to render the catalyst inactive. The initial rate of the catalyst prepared from this support was within the range of the values obtained from the study of the pretreatment of alumina described earlier in this chapter. It was expected that hydrogen would reduce the alumina and that the hydroxyl groups, thought to be the active sites responsible for the maximum activity in alumina supported catalysts, would be eliminated. The resultant activity seemed to indicate that this was not happening and that the activity of the alumina support was unaltered.

CHAPTER SIX

THE DISPROPORTIONATION OF PROPENE ON SUPPORTED ORGANOMETALLIC CATALYSTS OF MOLYBDENUM AND TUNGSTEN

6.1 Introduction

The use of supported organometallic catalysts in the disproportionation of olefins has not been reported in great detail. The carbonyls of molybdenum and tungsten have proved successful in effecting the disproportionation of propene when supported on γ-alumina[4,38,47,75]. In the light of these facts, it was decided to test the activity for disproportionation of certain substituted carbonyls of molybdenum and since the results obtained from supported molybdenum hexacarbonyl catalysts indicate that the active catalytic species is most probably non-carbonyl-containing, the activities of supported non-carbonyl complexes of molybdenum and tungsten were measured. The reproducible method of catalyst preparation described in Chapter 3 and Chapter 5 was used in the major part of this investigation.

6.2 Experimental

The experimental procedure for the study of the disproportionation reaction of propene has been described in Chapter 3, including details of the G.L.C. analysis and purification and storage of the reactants.

In the study of the organometallic catalysts, the supports used were γ-alumina and silica. The alumina support was pretreated in all cases at 573K for 1h and its surface area was

measured as 1.81×10^5 m^2kg^{-1}. The silica support (surface area 4.71×10^5 m^2kg^{-1}) was pretreated in all cases at 298K for 1h. The pretreatment conditions were determined from the results described in Chapter 5, which led to maximum activity of molybdenum hexacarbonyl catalysts supported on these oxides. The charcoal support (0.64×10^5 m^2kg^{-1}) was pretreated at 573K for 1h in vacuo. Most of the catalysts tested in this work were prepared by the "in situ" technique described in Section 3.3. Several catalyst samples were prepared by the dry-mixing and impregnation methods previously mentioned in Section 3.5. In the case of the "in situ" preparations, cyclohexane was the solvent used unless otherwise stated.

The samples (10^{-4}kg) prepared by the "in situ" technique were prepared in such a way that the "molarity" of the complex initially on the support was the same in all cases, and equivalent to the 10% $Mo(CO)_6$ catalyst. This allowed a direct comparison of each sample in terms of the number of molecules available for each site on the support. After impregnation of the solution of the organometallic compound on the support for 45 mins, the catalyst samples were heated in vacuo at 373K for 1h. In some cases, the catalysts were activated at higher temperatures than 373K before reaction. The samples prepared by the "in situ" technique were exposed to 3.33kNm^{-2} propene at 298K and the activity was taken as a measure of the initial rate of disappearance of propene.

In the case of the dry-mix and impregnation samples (5×10^{-4}kg), the γ-alumina support was pretreated at 673K for 1h, and cooled in air before impregnation or dry-mixing. After

activation at 373K for 1h, the activity was measured from the initial rate of disproportionation of 1.06kNm^{-2} of propene at 289K. These samples were 5% by weight complex:support ratio.

The measurement of the initial rates of disproportionation and the limitations imposed on such measured activities are described in Section 5.2.

6.3 Results

6.3.1 Substituted Molybdenum Complexes as Catalysts

The catalyst samples outlined in this section were prepared by the dry-mixing and the impregnation techniques detailed in Section 3.2.

Cycloheptatriene $Mo(CO)_3$ supported on γ-Al_2O_3

This organometallic complex was found to be only sparingly soluble in the more common hydrocarbon solvents and dry-mix preparations were tested for activity. The catalyst samples were activated at 360K and the initial rates of disproportionation were measured to be 0.2% min^{-1} and 0.1% min^{-1}.

Norbornadiene $Mo(CO)_4$ supported on γ-Al_2O_3

This complex was dissolved quite readily in acetone and a sample was prepared by impregnation and activated at 350K. There was no apparent activity for propene disproportionation. A dry-mix sample was found to exhibit an initial rate of 0.02% min^{-1} after activation at 346K.

Cyclopentadiene $Mo(CO)_3]_2$ supported on γ-Al_2O_3

Three separate catalyst samples were prepared by impregnation using acetone as solvent and activation at 368K. No disproportionation was observed at reaction temperatures as high as 343K.

Triphenylphosphine $Mo(CO)_5$ supported on γ-Al_2O_3

This catalyst was found to be mildly active (initial rate ~0.01% min^{-1}) at a reaction temperature of 343K. No disproportionation products were observed at 298K.

N-methylpyridiniumiodopentacarbonylmolybdate(0) on γ-Al_2O_3

An initial rate of disproportionation of 0.08% min^{-1} was measured for this catalyst, prepared under an atmosphere of nitrogen using tetrahydrofuran as solvent. A dry-mix sample was prepared again under nitrogen and initial rates of 0.12% min^{-1} and 0.06% min^{-1} were measured after catalyst activation at 373K. After activation of the catalyst at 473K, an initial rate of 0.25% min^{-1} was observed.

$Mo(CO)_5PH_3$ supported on γ-Al_2O_3

A catalyst sample was prepared by the dry-mixing technique and an initial rate of 0.05% min^{-1} was measured after catalyst activation of 373K.

$Mo(C\,Cl_2 = CHCl)(CO)_5$ supported on γ-Al_2O_3

This grey-coloured complex which was of uncertain composition

showed only one band in the carbonyl stretching region, but a dry-mix sample of the catalyst showed an activity for propene disproportionation measured as 0.9% min^{-1}.

Toluene $Mo(CO)_3$ supported on γ-Al_2O_3

A dry-mix preparation of this catalyst was activated at 343K and an initial rate of 0.4% min^{-1} was measured at 298K.

Mesitylene $Mo(CO)_3$ supported on γ-Al_2O_3

An initial rate of 0.8% min^{-1} was measured for a dry-mix sample activated at 358K.

$MoCl_5$ supported on γ-Al_2O_3

A dry-mix catalyst, prepared under nitrogen and activated at 373K, was found to be inactive.

$Mo_2(acetate)_4$ supported on γ-Al_2O_3

A dry-mix catalyst was activated at 373K and an initial rate of disproportionation of 0.01% min^{-1} was measured at 298K. After evacuation of the sample at 313K, the initial rate was recorded as 0.15% min^{-1}. The sample was treated with 1.33kNm^{-2} of 3,3,3-trifluoropropene at 298K for 2h and after evacuation at 313K for 1h, an initial rate of disproportionation of 0.31% min^{-1} was calculated. No disproportionation of the fluorinated olefin was detected.

6.3.2 Arene Complexes of Molybdenum as Catalysts

After the development of the reproducible "in situ" technique it was decided to re-examine the activities of the arene molybdenum tricarbonyl catalysts by this new method. The activities of these catalysts, prepared by the dry-mixing technique, are presented in Section 6.3.1. It was found that these organometallic complexes were very soluble in their parent solvent, e.g. mesitylene molybdenum tricarbonyl was dissolved in mesitylene before impregnation on alumina which had been pretreated at 573K for 1h. The catalysts were prepared as 10% samples by weight (complex:support ratio) - the molecular weights of the complexes were very similar to that of the molybdenum hexacarbonyl. The initial rates of disproportionation of 3.33kNm^{-2} propene on the catalysts are presented in Table 6.1. Also included in the table are activities for molybdenum hexacarbonyl catalysts.

TABLE 6.1

Activities of Catalysts $LMo(CO)_3$ *

	Initial Rate/(% min^{-1})	
L	1st Run	2nd Run
toluene	0.60, 0.53, 0.45	1.10, 1.25, 0.85
mesitylene	0.75, 0.56, 0.50	0.60, 0.80, 0.70
p-xylene	0.60, 0.30, 0.30	1.20, 2.50, -
$(CO)_3$	1.00, 0.78, 1.20	- , 1.50, -

* All catalysts supported on γ-alumina pretreated at 573K for 1h and activated at 373K for 1h (Chapter 5). Activities obtained from second runs on the catalyst samples are initial rates measured after evacuation of sample for 2h at 313K *in vacuo*.

6.3.3 Supported Molybdenum and Tungsten Complexes as Catalysts

Table 6.2 contains the result of the reaction of 3.33kNm^{-2} propene on 10^{-4}kg samples of the catalysts activated at 373K for 1h. The activities were measured in the usual manner with second order reversible rate equations used to determine the rates of reaction proceeding faster than ~1% min^{-1}. After first runs, most of the samples were evacuated at 473K for 1h and the activity for disproportionation of 3.33kNm^{-2} propene was measured. As indicated in Section 6.2, the catalyst samples were prepared to allow comparison with a catalyst sample of 10% $Mo(CO)_6$:support (by weight). The tungsten neopentyl complex was not a pure compound - it resembled the molybdenum species but was not isolable[98].

6.3.4 Study of Supported Hexamethyltungsten Catalysts

10% hexamethyltungsten catalysts (by weight), supported on alumina and silica, were tested for activity for propene disproportionation. The weight of hexamethyltungsten was estimated from the NO adduct $W(CH_3)_4[ONN(Me)O]_2$. The activities of the catalyst samples (10^{-4}kg) were calculated in the normal manner and are displayed in Table 6.3. For extremely rapid initial rates of disproportionation which were most probably diffusion-affected, it was not possible to calculate initial rates with the utmost accuracy. The charcoal supported catalyst showed no detectable activity for disproportionation after 6h of reaction.

TABLE 6.2

Catalyst	Initial Rate/(% min^{-1}) *	
	373 Activation	473 Activation
$Mo_2(CH_2SiMe_3)_6/SiO_2$	0.80	4.2
$Mo_2(CH_2SiMe_3)_6/Al_2O_3$	1.82	1.40
$W_2(CH_2SiMe_3)_6/SiO_2$	0.47	
$W_2(CH_2SiMe_3)_6/Al_2O_3$	1.43	3.64
$Mo_2(CH_2CMe_3)_6/SiO_2$	3.50	6.4
$Mo_2(CH_2CMe_3)_6/Al_2O_3$	1.79	1.18
$W_2(CH_2CMe_3)_6/SiO_2$	3.84	10^{-3}
$W_2(CH_2CMe_3)_6/Al_2O_3$	4.2	0.77
$W_2(CH_2CMe_3)_6$/Charcoal	No disproportionation	

* Propene pressure 3.33kNm^{-2}; T = 298K.

TABLE 6.3

Activities of Supported Hexamethyltungsten Catalysts*

Catalyst	Activation Temperature of Catalyst/K			
	298	373	473	573
$W(Me)_6/SiO_2$	0.05	3.18	3.10	-
$W(Me)_6/SiO_2$		7.0	9.0	8.0
$W(Me)_6/SiO_2$		5.3	-	-
$W(Me)_6/Al_2O_3$		3.64	3.10	-
$W(Me)_6$/Charcoal		‡		
$W(Me)_4[ONN(Me)O]_2$			10^{-3}	

* Initial rate/(% min^{-1}) measured from the rate of disappearance of 3.33kNm^{-2} propene at 298K.

‡ No reaction after 6h.

6.4 Discussion

The results obtained from the substituted molybdenum complexes supported on alumina indicate that in most cases the catalyst was active for disproportionation. Bearing in mind the difficulties encountered in comparing the activities of catalyst samples which were prepared by the impregnation or dry-mix techniques, it would not be feasible to draw strict conclusions from such results. It was originally intended to contrast the activities of the supported catalysts by variation of ligand(s). The irreproducibility of these preparations did not allow an accurate assessment of the results obtained from these catalysts.

However, the fact that these catalysts are active for disproportionation would seem to suggest that, in view of the work carried out on supported molybdenum hexacarbonyl[80,90] using e.s.r. and infrared techniques, the same active species is probably generated in each case, i.e. a coordinatively unsaturated species with molybdenum in a higher oxidation state than zero[90]. The active catalyst is thought to contain no molybdenum-carbon bonds. It is probable that similar species are obtained under more extreme conditions from molybdenum (VI) oxide catalysts supported on alumina.

Any variation in the activity of the disproportionation catalyst obtained from these complexes could probably be attributed to a combination of several factors:

(a) Experimentally, the same weight of compound was taken for support on the alumina, hence, since different molecular weights are involved, then if the same active catalyst is formed

it would be reasonable to expect different amounts of active species to be generated.

(b) In each case, the catalyst was activated at a temperature just below that of the melting point of the complex. Due to the variation in melting points, it is probable that with the catalysts activated at different temperatures, different amounts of active species are formed.

(c) Compounds will possess different tendencies to undergo oxidation and concomitant Mo-C bond cleavage which, together with (b) will again produce different amounts of the active species.

There is no direct evidence to support the formation of the same active species, but if the carbonyl ligand is displaced so readily for molybdenum hexacarbonyl, it is quite likely that the diene, arene complexes will be similarly affected when supported on alumina.

The molybdenum pentacarbonyl iodide complex which showed a reasonable activity for disproportionation when supported on alumina is reported as active for disproportionation in the homogeneous reaction, olefin metathesis[99].

The activity of the supported molybdenum acetate catalyst confirms the suggestion that the active catalytic species contains no carbonyl ligands. This interesting result dismisses the impression that the carbonyl catalysts held special attributes for activity in the disproportionation reaction. This demonstrates that the role of all the low valent molybdenum complexes is simply to provide a facile means of generating the active species. The activities of other non-carbonyl complexes are presented in Section 6.3.3, and will be discussed later.

The work on the arene complexes was repeated using the "in situ" technique and a greater degree of reproducibility was obtained. Originally the object of the investigation into the activities of such catalysts was to detect possible changes in the activity with variation in ring type, viz., number of methyl substituents. The results appear to indicate that the activity is independent of number of methyl groups, since all catalysts were of comparable activity. Since the hexacarbonyl catalyst contains no carbonyls, it is likely that with the arene complexes, the catalyst will contain no arene. Thus, given the same catalyst activation temperature, it would be expected that the initial rates would be independent of ring type. Oxidation of the catalyst to the active species will probably occur in a similar fashion in all three cases.

The results obtained from the tungsten and molybdenum complexes supported on silica and alumina further support the previous findings that the catalyst need not be carbonyl-containing for the generation of the active species. From these results it is noticeable that the activity of the tungsten catalysts is comparable with that of the molybdenum catalysts. This was not indicated in the preliminary study of tungsten hexacarbonyl supported on alumina[75], where the activities for propene disproportionation were slower than those observed for the molybdenum hexacarbonyl catalyst by a factor of 10^3.

The activities of the molybdenum and tungsten neopentyl catalysts follow the trend observed in the work carried out on molybdenum hexacarbonyl (Chapter 5). The silica supported catalysts were more active than those supported on alumina and

the activities of these catalysts were comparable with those measured for molybdenum hexacarbonyl. In the light of these findings, it would be reasonable to suggest that the generation of the active species followed a similar pattern to that of molybdenum hexacarbonyl, i.e. decomposition of the complex on the support followed by oxidation to the active species. It is interesting to note the high activity for the tungsten neopentyl catalyst supported on alumina may be due to the impurity of that complex and the difficulty in preparation.

In the case of the metal alkyls, it is known in the case of lithium and magnesium[100,101] that they react with silica:

$$\equiv Si-OH + LiCH_3 \longrightarrow \equiv Si-O-Li + CH_4$$

Since molybdenum and tungsten alkyls are susceptible to hydrolysis[102], then it is feasible to anticipate a similar reaction taking place with these complexes supported on silica and alumina, where hydroxyl groups are present in each case. This allows the initial linkage of the transition metal to the support.

The lower activities of the trimethylsilylmethyl catalysts compared to the neopentyl samples can be explained as a result of their marginally higher thermal stability, which would render these complexes less likely to interact with the support in a manner likely to generate the active catalytic species. The results show that for the trimethylsilylmethyl catalysts the alumina supported catalysts were more active than the samples supported on silica. This appeared to reverse the trend obtained from the molybdenum hexacarbonyl catalysts (Chapter 5) and this

phenomenon may be due to an interaction between the trimethylsilylmethyl ligand and the alumina support. Silation reactions have been observed on surfaces using compounds such as Me_3SiCl[103,104] and Me_3SiOEt[105], but in order to silate with less active silyl compounds, e.g. tetramethylsilane[106], relatively high temperatures are required. No further experiments were carried out to investigate this phenomenon or confirm that silation was in fact taking place.

It was observed (Chapter 5) that samples of molybdenum hexacarbonyl supported on silica-alumina possessed activities intermediate between silica and alumina supported samples. However, this silica-alumina support was prepared by co-precipitation and not by surface coating and these results would be expected.

The hexamethyltungsten complex, when supported on silica, produced the most active catalyst of those studied for propene disproportionation. The unstable nature of this complex meant that, after impregnation, any excess hexamethyltungsten would have thermally decomposed, even before activation of the catalyst at higher temperatures. It is noticeable that catalyst activation at room temperature was not sufficient to generate a catalyst of high activity. Activation at 373K or higher was necessary to produce a sample of the high activity observed for molybdenum hexacarbonyl results (Chapter 5) and from the organometallic catalysts discussed in this chapter, it is interesting to observe that in the hexamethyltungsten case, an active catalyst was derived from a complex in which the metal was formally in an oxidation state of six. The alkyl dissociation of copper and silver complexes to form reduced metal species

and alkyl radicals has been studied[107] and it is likely that hexamethyltungsten would decompose in a similar fashion, the tungsten metal being reduced to a lower formal oxidation state, possibly W (IV). There has been no e.s.r. evidence for this species but preliminary infrared investigations on the supported hexamethyltungsten catalysts[108] indicate that, at room temperature, the methyl groups were still bonded to the supported catalyst, probably to tungsten. On heating, the e.s.r. spectrum showed that methyl radicals were formed[109] and a reductive elimination of the methyl ligands is presumed to occur. It would not be necessarily true that the active catalyst contained any methyl groups attached to the tungsten metal.

The failure of the tungsten adduct, $W(Me)_4[ONN(Me)O]_2$, to generate an active catalyst was quite surprising, although recent work in this Department has shown that nitric oxide is capable of poisoning molybdenum hexacarbonyl disproportionation catalysts. It is conceivable that decomposition of the complex on the support caused loss of NO-type ligands which in turn poisoned the sites active for propene disproportionation.

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